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The structure of overlayers. II. Si on Mo[001]

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The Mo{001}1 × 1-Si structure formed upon adsorption of a monolayer of Si on a clean Mo{001} surface is investgated by means of low-energy electron diffraction (LEED). Diffracted beam intensities are calculated with the layer–Korringa-Kohn-Rostoker method for different models and compared with extensive experimental data. Good agreement between calculated and observed LEED spectra for six nondegenerate beams at an angle of incidence of 8° and for four nondegenerate beams at an angle of incidence of 21° is found for a model in which the Si atoms are adsorbed in the fourfold pyramidal hollows formed by four adjacent Mo atoms on the Mo{001} surface. The distance between the plane of adsorbed Si atoms and that of the top layer of Mo atoms is 1.16 ± 0.1 Å and the Si-Mo bond length is 2.51 ± 0.05 Å. The effects caused by different choices of a number of structural and nonstructural parameters in the calculated LEED spectra are discussed, and the results of calculations based on "wrong" models are presented for comparison. The importance of studying many beams and several angles of incidence is emphasized.

I. INTRODUCTION

Study and understanding of the low-energy-electron-diffraction (LEED) experiment have advanced to the point where the determination of surface structures is feasible through an analysis of the diffracted intensities. Recent years have witnessed the structure determinations of a number of surfaces of clean metals and a few insulators, as well as of several overlayer systems.[1] Among the latter, the one that has attracted most attention is the superstructure commonly labeled $c(2\times 2)$ on face-centered-cubic {001} surfaces, which can be regarded as a doubling of the periodicities in the plane of the surface and a centering of the two-dimensional unit cell (the crystallographically correct[2] Wood's shorthand notation[3] for this superstructure is, however, $\sqrt{2}\times\sqrt{2}-45°$). The $c(2\times 2)$ type of superstructures is in fact one of the simplest to handle theoretically, as it involves only one extra (or fractional-order) beam per unit mesh; moreover, it seems to form readily when foreign atoms are adsorbed on fcc {001} surfaces. In the overwhelming majority of the cases investigated so far for the $c(2\times 2)$ structure, the adatoms were found to be located in the fourfold coordinated pyramidal hollows on the fcc {001} surface, which would harbor substrate atoms if the substrate crystal were to grow. Except for the few cases in which the adatoms are believed to penetrate the surface layer and form ordered or disordered alloys, the latter seems in fact to be characteristic of all overlayer systems on any of the surfaces studied to date.

The present paper reports the results of a structure analysis of an overlayer adsorbed on a body-centered-cubic {001} surface, namely, the Mo{001} surface. The adsorbate is silicon, and the experimental evidence suggests that the system under investigation consists of a single monolayer of Si atoms adsorbed on the Mo{001} surface.[4] The novelty of the structure determination reported here is that the periodicity of the overlayer is the same as that of the substrate, so that there are *no* fractional-order beams—in Wood's shorthand notation, the structure is labeled Mo{001}1 × 1 – Si.

In general, the absence of fractional-order beams makes the structure analysis somewhat more difficult, since all conclusions must be drawn from changes in the integral-order beams. In fact, when fractional-order beams are present, the analysis usually starts with a study of such beams only. If, for a given model, no match is found between theoretical and experimental fractional-order spectra, the model is probably wrong no matter how good the match of the integral-order beams may be. If, on the other hand, calculated and observed fractional-order spectra show good correspondence, the postulated model is likely to be correct even if the integral-order beams show less good correspondence. It is possible, in fact, that the overlayer structure under investigation does not cover the whole area illuminated by the beam, i.e., that because of imperfections the surface consists of regions with a 1 × 1 or the "clean" structure and regions with the larger-mesh overlayer structure. In these cases, some suitable weighted average among integral-order spectra of a 1 × 1 structure or the clean substrate surface and integral-order spectra of the overlayer structure is likely to produce curves which match the experiment satisfactorily[5] with-out affecting the correspondence of fractional-order beams. In overlayer structures of the 1×1 type, the advantage of having beams (the fractional-order ones) that are insensitive to the extent of surface coverage by the desired structure is missing. In addition, only some of the diffracted beams of the clean surface may be noticeably affected by the presence of the overlayer, while others may exhibit only minor changes. Hence, the analysis of a 1×1 structure requires that more care be taken in examining the available beams and that a greater number of beams be studied so that ambiguities can be resolved. Experimentally, one should try to insure that the *whole* surface is covered with the desired structure, but the possibility should nevertheless be kept in mind that, for example, "clean" regions or multilayer-absorption regions may coexist with the desired structure on the surface, so that some suitable averaging process among structures may be necessary to produce agreement between calculations and observations. In the Mo {001} 1×1 – Si structure discussed below, the experimental evidence pointed toward monolayer coverage of the substrate surface,[4] and hence no averaging with clean regions was expected to be necessary, and in fact none was needed. In Sec. II, we review briefly the experimental aspects of this study. In Sec. III, we present and discuss the results of the structure analysis.

II. EXPERIMENTAL PROCEDURES

The Mo{001} surface was cleaned *in situ* with successive argon-ion bombardment and annealing treatments as described elsewhere.[6] Silicon was deposited on it at the rate of 0.2 to 0.5 monolayer-equivalents per minute by sublimation of a high-purity single-crystal heated resistively to 1300–1400 °C at pressures of $(1-5)\times10^{-10}$ Torr.[7] The LEED and Auger-electron-spectroscopy (AES) observations of the Si-covered Mo{001} surface are described elsewhere.[4] The brightness of the diffraction spots formed on the fluorescent screen was measured with a spot photometer and converted to electron-current units by means of calibration with a movable Faraday cage. The measured diffracted intensities were then normalized to constant incident current and corrected for a contact-potential difference of 3.9 eV. Adjustments and measurements of the angle θ between the incident electron beam and the normal to the surface, and of the azimuth angle ϕ between the projection of the incident beam onto the surface and the k_x axis of the reciprocal net were carried out as described elsewhere.[8]

Two sets of intensity data were collected. One set, for $\theta=8°$ and $\phi=0°$, consists of six nondegenerate beams; the other, for $\theta=21°$ and $\phi=0°$, of four nondegenerate beams. The beams were indexed on the basis of the primitive-square-unit mesh characteristic of body-centered-cubic {001} surfaces.

III. STRUCTURE ANALYSIS OF Mo{001}1x1-Si

The first step in the lengthy process of structure analysis is the choice of a model for the structure to be determined, i.e., the choice of the parameters to be used in the calculations of LEED spectra. For convenience, we divide the parameters into two groups: (i) the group of "structural" or "geometrical" parameters, which comprise all distances between atoms and between planes of atoms, and (ii) the group of "nonstructural" parameters, i.e., the real and imaginary parts of the complex potentials of both substrate and surface layer (or overlayer), the values of the "inner potentials" V_0^B and V_0^S in the bulk and in the surface, respectively, and the parameters that describe the vibrational motions of both substrate and surface atoms (e.g., the Debye temperatures Θ_D^B and Θ_D^S of bulk and surface, respectively).

The nonstructural parameters are found as follows. In a case, such as the present, of an overlayer system, all parameters that refer to the substrate are known from an analysis of the clean surface of the substrate. Thus, the real part of the substrate potential is the self-consistent band-structure-type potential used in the analysis of the clean Mo{001} surface.[6] Similarly, the imaginary part of the substrate potential β^B, the inner potential of the substrate V_0^B, and the Debye temperature Θ_D^B of the substrate, are obtained from the clean-surface study. In the present case, the values are: $\beta^B=4$ eV (independent of energy), $V_0^B=16$ eV (although in the clean-surface analysis V_0^B was taken to be dependent on energy, varying from 16 to 13 eV in the range from 20 to 150 eV), and $\Theta_D^B=360$ °K. The corresponding quantities of the overlayer (β^S, V_0^S, and Θ_D^S) were initially taken to have the same values as their bulk counterparts. The real part of the potential for the Si overlayer was calculated from the superposition of atomic-charge densities for a three-dimensional Si crystal with fcc structure and lattice parameter 4.05 Å. This method of calculating potentials for overlayers has proven very successful in a few recently reported structure analyses.[9]

The structural parameters depend directly upon the postulated atomic arrangement at the surface. Assuming that the adatoms lie *over* (rather than *within*) the top layer of substrate atoms, one can construct a number of structural models that are all consistent with 1×1 symmetry and periodicity of the LEED pattern observed. Some of these models are depicted schematically in Fig. 1, where the empty circles represent substrate atoms and

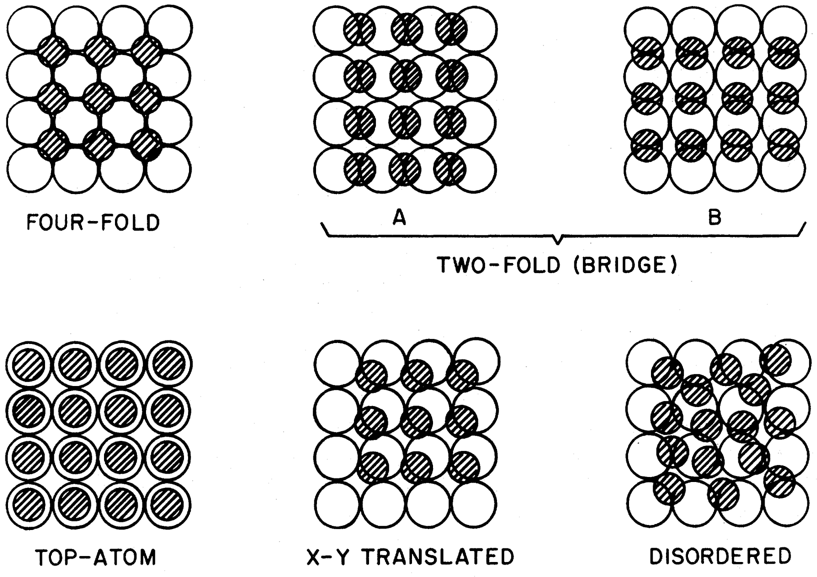

FIG. 1. Schematic models for an overlayer structure with the same periodicity as the substrate (so-called 1×1 structure). In the twofold model, it is generally assumed that both *A* and *B* domains are present in equal proportions. Hence, intensity calculations must be first carried out for *A* and *B* domains separately and then averaged. More complicated averaging would be required by the *x*-*y* translated model.

the hatched circles represent adatoms (in the present case, Mo and Si atoms, respectively). In the so-called "fourfold" model, the Si atoms are adsorbed into the fourfold pyramidal hollows formed by four adjacent Mo atoms. In the "twofold (or bridge)" model, the Si atoms are adsorbed in the twofold symmetrical positions across two adjacent Mo atoms. There are two nonequivalent possibilities (*A* and *B*) for this model, one obtained from the other by a rotation through 90°; in general, such an overlayer structure will contain both *A* and *B* "domains" in equal proportions. Hence, two calculations must be carried out, one for each domain, and then averaged to obtain spectra that can be compared with the experiment. A third model is the so-called "top-atom" model, in which the adatoms are located directly on top of the underlying substrate atoms. A fourth and a fifth model, computationally more difficult to handle, are the "x-y translated" overlayer model in which the adsorption sites are in general positions (requiring the averaging of the results from four domains), and the "disordered" model, respectively, depicted in Fig. 1.

An additional unknown in all models, of course, is the z coordinate of the adatoms (the z axis is taken to lie along the surface normal), which determines the spacing d_z^S between the overlayer and the top layer of substrate atoms. In the present study, the models that were investigated are the fourfold, the twofold and the top-atom models, each for a variety of d_z^S values. No other model needed consideration because satisfactory agreement between theory and experiment was found for the fourfold model. All calculations were carried out with the layer-Korringa-Kohn-Rostoker method described elsewhere,[10] and involved eight phase shifts and 38 or 48 beams. In Sec. III A, we describe first the characteristics of the fourfold model and present all the evidence for its selection as the correct one. Then in Sec. III B we discuss the effects of changes in the values of some parameters and report, for the sake of comparison, some of the results obtained with "wrong" models.

A. Best values of the parameters

In the model we believe is best for the Mo{001} 1×1-Si structure, the Si atoms are adsorbed on the fourfold symmetrical hollows of the Mo{001} surface in such a way that the Si-Si interatomic distances are equal to the lattice constant in the Mo{001} plane, i.e., 3.146 Å, and the distance between Si and Mo layers is $d_z^S = 1.16$ Å, to be compared with Mo-Mo interplanar distances of 1.57 Å in bulk Mo. Thus, the Si-Mo interatomic distance is 2.51 Å, to be compared with a Mo-Mo interatomic distance, in the Mo crystal, of 2.725 Å. Note that the sum of the covalent radii[11] of Si (1.17 Å) and Mo (1.37 Å) is 2.54 Å. The nonstructural parameters used in the calculations were, in addition to the potentials for the substrate and the overlayer mentioned above, $V_0^S = V_0^B = 16$ eV, $\Theta_D^S = \Theta_D^B = 360$ °K, $\beta^B = 4$ eV, and $\beta^S = 2$ eV. Figures 2-4 show the comparison between observed and calculated spectra for six nondegenerate beams at $\theta = 8°$, and Figs. 5 and 6 do the same for four nondegenerate beams at $\theta = 21°$.

Quantitative agreement among absolute values of observed and calculated intensities of any given beam is not better than a factor of 15 or 20, owing

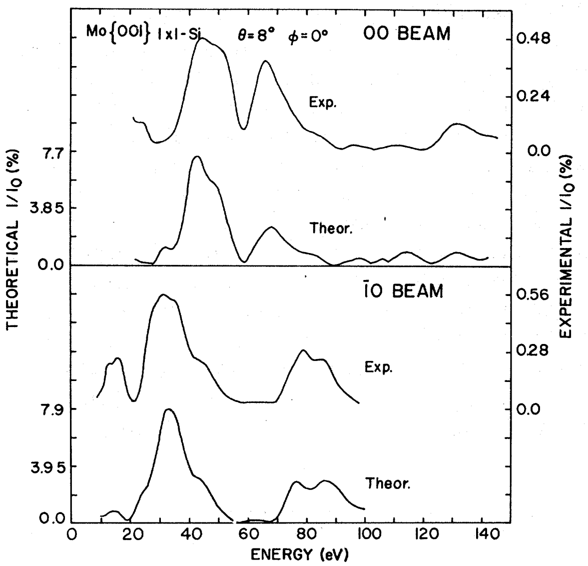

FIG. 2. Experimental spectra of the Mo{001} 1×1-Si structure and corresponding theoretical spectra calculated for the "fourfold" model depicted in Fig. 1: $\theta = 8°$, $\phi = 0°$. Top panel: 00 spectrum. Bottom panel: $\bar{1}0$ spectrum.

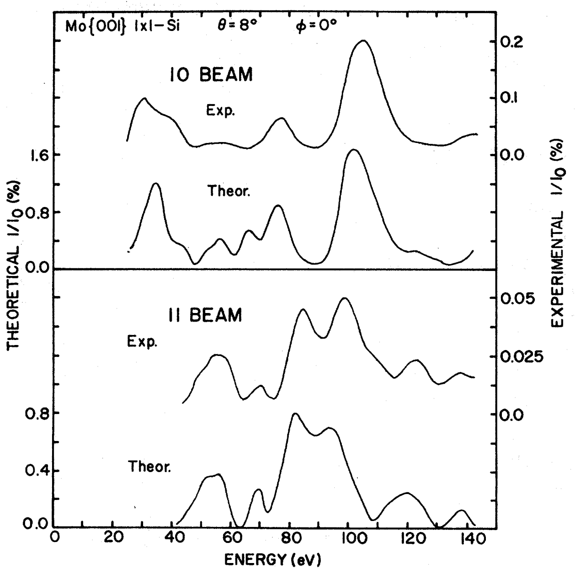

FIG. 4. Experimental spectra of the Mo{001} 1×1-Si structure and corresponding theoretical spectra calculated for the fourfold model depicted in Fig. 1: $\theta = 8°$, $\phi = 0°$. Top panel: 10 spectrum. Bottom panel: 11 spectrum.

to the uncontrollable effect of surface roughness.[12] However, the agreement among peak shapes, peak widths and peak heights is in general quite satisfactory. Peak positions coincide in general within 4 or 5 eV (with two exceptions, one for the 01 beam for $\theta = 21°$ at 28 eV and the other for the 11 beam also for $\theta = 21°$ at 125 eV), but exhibit the characteristic trend, observed elsewhere,[6,13] that could be explained and reproduced by an energy-dependent inner potential, not adopted here. Although the agreement between theory and experiment is better for some beams than for others,

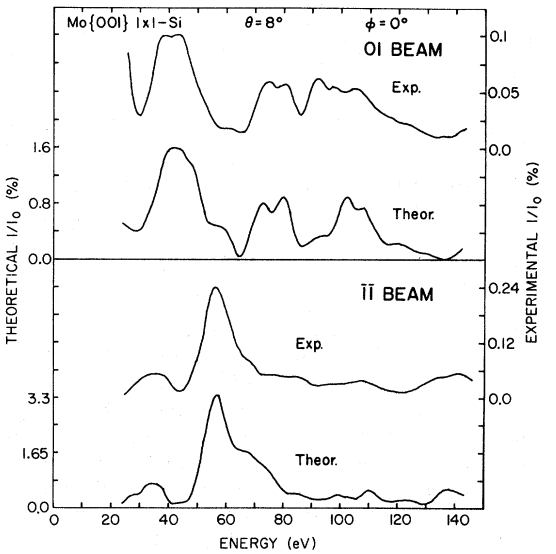

FIG. 3. Experimental spectra of the Mo{001} 1×1-Si structure and corresponding theoretical spectra calculated for the "fourfold" model depicted in Fig. 1: $\theta = 8°$, $\phi = 0°$. Top panel: 01 spectrum. Bottom panel: $\bar{1}\bar{1}$ spectrum.

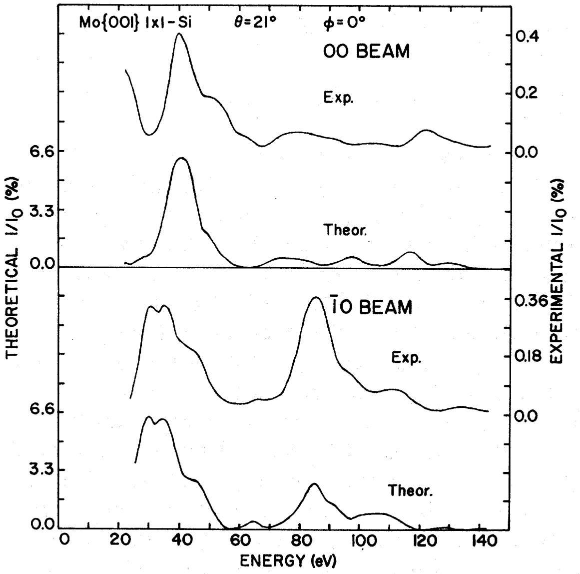

FIG. 5. Experimental spectra of the Mo{001} 1×1-Si structure and corresponding theoretical spectra calculated for the fourfold model depicted in Fig. 1: $\theta = 21°$, $\phi = 0°$. Top panel: 00 spectrum. Bottom panel: $\bar{1}0$ spectrum.

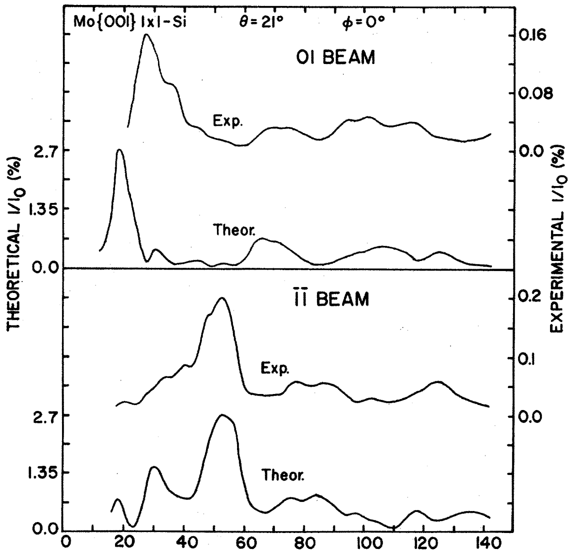

FIG. 6. Experimental spectra of the Mo{001} 1×1-Si structure and corresponding theoretical spectra calculated for the fourfold model depicted in Fig. 1: $\theta=21°$, $\phi=0°$. Top panel: 01 spectrum. Bottom panel: $\bar{1}\bar{1}$ spectrum.

and better in some portions of a given spectrum than in others, the overall correspondence among ten beams at two angles of incidence gives us sufficient confidence to claim that the observed Mo {001} 1×1-Si structure consists indeed of a single monolayer of Si atoms adsorbed on the Mo{001} surface (as inferred from the experimental observations reported earlier[4]), and that the atomic arrangement is the one given by the model described above.

B. Effect of parameter variation

The analysis of the structure of the clean Mo {001} surface[6] indicates that the top layer of atoms is contracted about 11% as compared to the bulk interplanar spacing along ⟨001⟩. Our calculations indicate that such a contraction does *not* persist when Si is adsorbed onto the 1×1 structure discussed here. The agreement between theory and experiment exhibited in Figs. 2–6, which were obtained assuming an unrelaxed Mo substrate, is noticeably worsened by the assumption that the top Mo layer is contracted 11%, and slightly worsened by the assumption that the same contraction is of 5%. We conclude, therefore, that the adsorption of one monolayer of Si atoms relaxes the Mo{001} surface to the extent that the interplanar distances in the direction perpendicular to the surface become equal to those in the interior, at least within less than 5%.

The distance d_z^S between the plane of the adsorbed Si atoms and that of the underlying Mo atoms has been fixed at the value 1.16 Å after consideration of the *overall* correspondence between theory and experiment. Calculations of the LEED spectra have been carried out for several values of d_z^S differing from one another by 0.025 A. Some beams are rather insensitive to changes of d_z^S. Of those which are sensitive to such changes, some may exhibit better correspondence with experiment at different values of d_z^S than others. Figure 7 shows an example of this case: For the 00 beam at $\theta=8°$, the spectrum calculated for $d_z^S=1.21$ Å is worse, as far as agreement with experiment is concerned, than that calculated for $d_z^S=1.16$ Å, but that calculated for $d_z^S=1.10$ Å is better. On

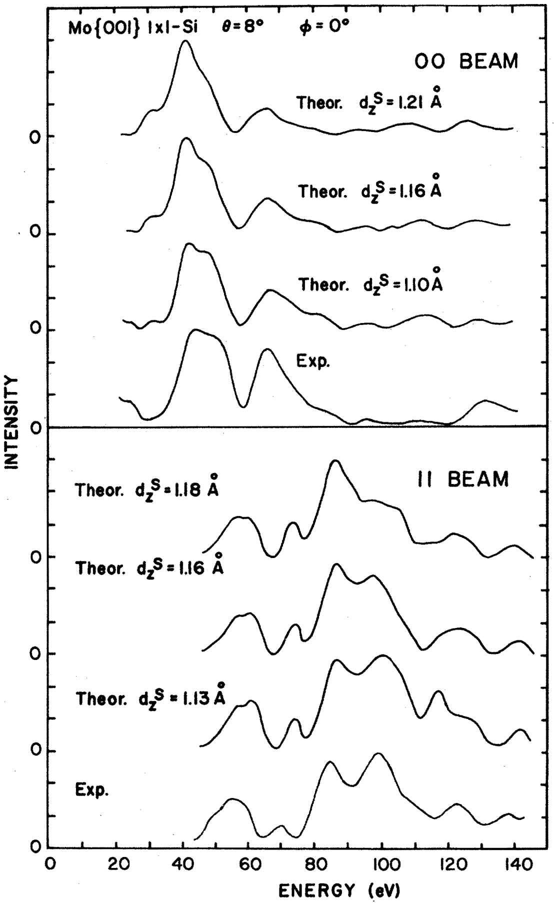

FIG. 7. Effect of changes in the distance d_z^S between the plane of adsorbed Si atoms and the uppermost plane of Mo atoms in the Mo{001} 1×1-Si structure (fourfold model). Top panel: 00 spectra—the curve calculated for $d_z^S=1.10$ Å fits the experiment somewhat better than the curves calculated for either $d_z^S=1.16$ Å or $d_z^Z=1.21$ Å. Bottom panel: 11 spectra—the curves calculated for $d_z^S=1.16$ Å and $d_z^S=1.13$ Å fit the experiment equally well (and better than the curve calculated for $d_z^S=1.18$ Å) up to about 110 eV, but at higher energies, 1.16 Å is better.

the other hand, for the 11 beam at $\theta = 8^\circ$, the value $d_z^S = 1.18$ Å produces somewhat worse agreement with experiment than $d_z^S = 1.16$ Å, while $d_z^S = 1.13$ Å produces as good an agreement as 1.16 Å up to about 110 eV, but a worse one above that energy. Thus, the value 1.16 Å represents a compromise over all ten beams examined here, and the limits of error are somewhat better than ±0.1 Å. Correspondingly, the Si-Mo bondlength is 2.51±0.05 Å.

The effect of variation of the nonstructural parameters is exemplified by the spectra reproduced in Fig. 8. The strongest effect is produced by variations of the surface inner potential V_0^S, which may occasionally generate new peaks and annihilate or shift substantially existing ones, often in unpredictable fashion. Much less pronounced and more predictable are the effects caused by absorption (β^S) and thermal motion (Θ_D^S) in the surface layer. Increasing β^S attenuates and broadens all peaks, much in the way bulk absorption (β^B) does, but for $\beta^S \geqq 1$ eV, the effects of small changes (by a few eV) in β^S are hardly perceptible. Increasing the vibration amplitude of the surface atoms, i.e., decreasing the surface Debye temperature Θ_D^S, also attenuates the peaks, but attenuates those at lower energies more than those at higher energies. Again, for reasonable changes of the values, the effects on the calculated spectra seem to be minor, at least at energies larger than 20 or 30 eV. In the 00 and $\bar{1}0$ spectra depicted in Fig. 8, β^S is nearly constant, V_0^S is varied substantially (top three curves in each panel), and Θ_D^S is varied by more than a factor of 3 (bottom curve in each panel).

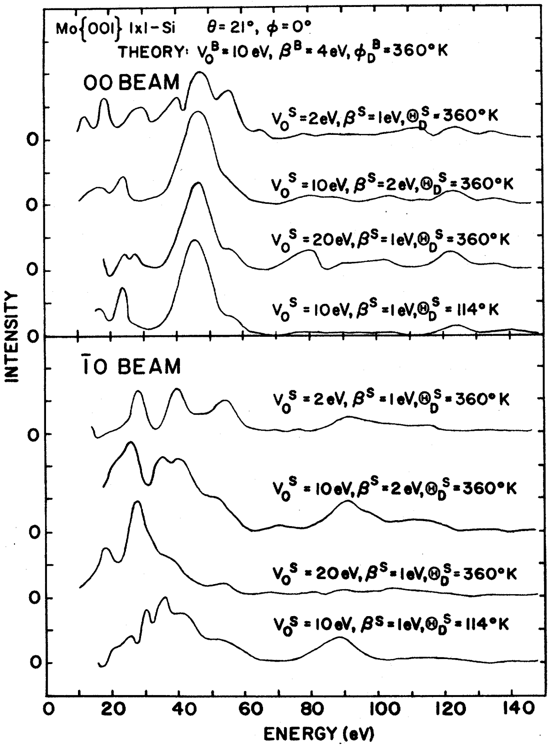

FIG. 8. Effects of nonstructural parameters on calculated spectra of the Mo{001} 1×1-Si structure (fourfold model). In the upper three curves in each panel the value of the surface Debye temperature Θ_D^S is held constant, the surface absorption parameter β^S is almost held constant, and the surface inner potential V_0^S is varied. In the bottom curves, Θ_D^S is also varied. Top panel: 00 spectra. Bottom panel: $\bar{1}0$ spectra. The intensity scale has been readjusted to make the largest peak in each spectrum approximately the same.

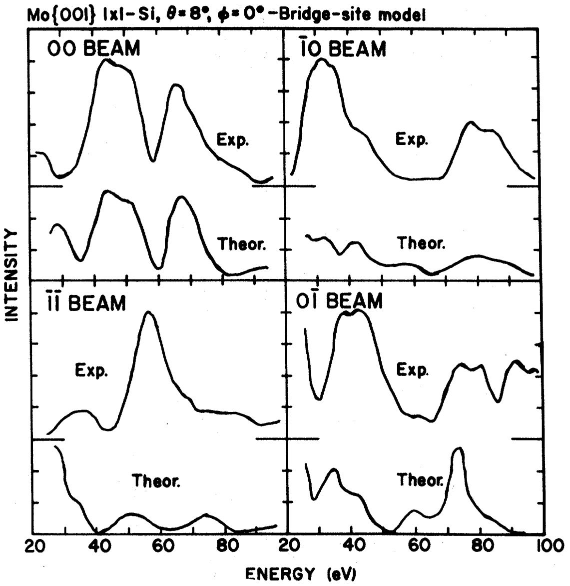

FIG. 9. Experimental spectra of the Mo{001} 1×1-Si structure and theoretical spectra calculated for the bridge-site model depicted in Fig. 1 ($d_z^S = 1.10$ Å, the curves presented here are averages of the A and B configurations). The 00 spectra show almost perfect correspondence, but the other spectra (only three of which are shown here), indicate that the model is wrong.

Our conclusion, from the limited experience acquired so far in the structure determination of clean metal surfaces and overlayer systems, is that variation of the nonstructural parameters may occasionally provide the finishing touch on an already substantial agreement between calculations and observations, but if the postulated structure model is wrong, it can never produce such agreement over a large number of beams. To feel confident in a structure determination, we believe that a substantial number of beams must be considered in carrying out a surface-structure analysis—certainly more than two. A confirmation of the latter statement is provided by a study of different models for a given structure. Figure 9 compares with experiment a few spectra calculated for the

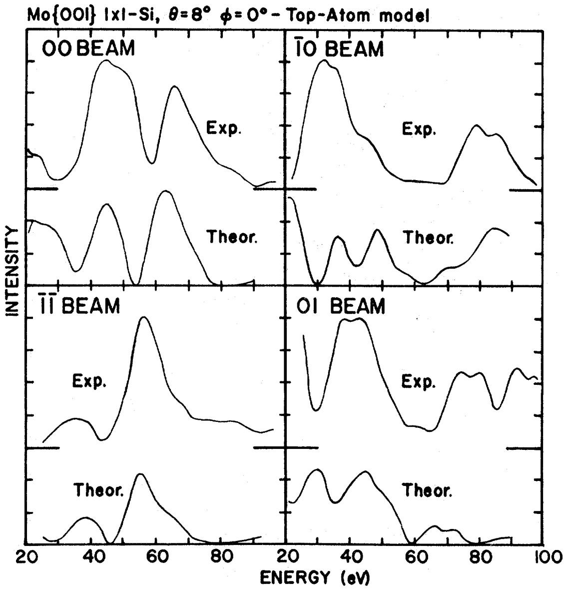

FIG. 10. Experimental spectra of the Mo{001} 1×1-Si structure and theoretical spectra calculated for the top-atom model depicted in Fig. 1 ($d_z^S = 1.74$ Å). The 00 spectra show moderate correspondence and the $\overline{1}\,\overline{1}$ spectra good correspondence, but the other spectra, two of which are shown here, make it impossible to accept the model as correct.

"bridge-site" model shown in Fig. 1, while Fig. 10 does the same for the top-atom model, also shown in Fig. 1. The bridge-site model produces a 00 spectrum that agrees almost perfectly with experiment (top left-hand panel in Fig. 9), much better, in fact, even than its counterpart of the right structure (Fig. 2). However, there is practically no correspondence between calculations and observations for the nonspecular beams considered in this analysis (only three of them are shown in Fig. 9), and therefore the postulated model must be discarded. The top-atom model, on the other hand, produces a 00 spectrum in mediocre agreement with experiment (top left-hand panel in Fig. 10) and a $\overline{1}\,\overline{1}$ spectrum in excellent agreement with experiment (bottom left-hand panel in Fig. 10), but produces also other spectra (only two of which are shown in Fig. 10) which are unacceptable with regard to the experiment, and must therefore also be discarded as wrong. Note that the spectra presented in Figs. 9 and 10 are those calculated for values of d_z^S which give "best" correspondence with experiment, these values being $d_z^S = 1.10$ Å for the bridge-site, and $d_z^S = 1.74$ Å for the top-atom model.

We conclude, therefore, by re-emphasizing the importance, for purposes of surface-structure analysis, of considering not only the specular beam but a substantial number of nonspecular beams as well.

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