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Abstract

The structures of the clean "(1x1)" and the "c(2x2)" sulfur-covered molybdenum (100) surfaces have been studied by low-energy electron diffraction (LEED) intensity analyses. It is found that the atoms in the top layer of both these surfaces probably reside at asymmetrical adsorption sites, destroying the perfect (1x1) and c(2x2) periodicities normally deduced from the LEED patterns. For clean room-temperature Mo(100), a slight preference is found for the topmost atoms to be displaced 0.13 ± 0.05 Å away from the centers of hollow sites of the second metal layer. This displacement occurs in the four equivalent <11> surface directions (diagonally in the square surface lattice), possibly randomly. The clean surface exhibits first, second and third interlayer spacing relaxations of -6% ± 1.5%, 2% ± 2% and 0.5% ± 3%, respectively, relative to the bulk interlayer spacing. In the "c(2x2)" sulfur overlayer, the sulfur atoms are found to reside away from the center of hollow sites by 0.20 ± 0.05 Å. This displacement occurs in the four equivalent <10> surface directions (parallel to the sides of the square metal lattice cells), possibly randomly. The sulfur-Mo interlayer spacing is 1.03 ± 0.02 Å , while the spacings between metal layers have relaxed closer to their bulk value, with a top metal-metal spacing still contracted by 3% ± 3%. The asymmetrical site gives rise to three different bond lengths between sulfur and molybdenum atoms: 2.33 and 2.58 Å for Mo atoms in the topmost metal layer, and 2.56 Å for Mo atoms in the second metal layer. In this case, no lateral Mo relaxations were investigated.

1. Introduction

The interaction of sulfur with transition metal surfaces has been studied by many groups. The molybdenum-sulfur system is especially interesting because of its application in hydrodesulfurization or hydrocarbon conversion reactions and in the design of sulfur-resistant catalysts. Many articles have been published on the clean and sulfur-covered Mo(100) surface.[1-16] Since the adsorption site of sulfur on such surfaces is quite important for catalytic processes, many of these studies were concerned with the determination of the structures of the clean surface and the adsorbed overlayer.

The clean Mo(100) surface is known to reconstruct in a complex manner at low temperatures[17], in a way reminiscent of the simpler c(2x2) reconstruction of W(100).[11,18] The Mo(100) reconstruction is thought to be an incommensurate version of the commensurate W(100)-c(2x2) structure.[19] The latter low-temperature ordered structure has been studied mainly by LEED,[11,18,20] x-ray diffraction[21] and theory[22,23]: it is thought to consist of displacements of top-layer atoms parallel to the surface in the <11> diagonal directions, in addition to possible interlayer relaxations. The room-temperature structures of W(100)[18] and of Mo(100)[11] yield apparent (1x1) LEED patterns, thought to be due to disordering rather than removal of the parallel atomic displacements. This has been confirmed for W(100) by a recent LEED analysis,[24] which showed that the top-layer W atoms shift laterally by about 0.16Å along the <11> directions. It has been proposed also on theoretical grounds that the high-temperature "(1x1)" structure of Mo(100) could be of this type as well.[16] We shall use quotations marks, as in "(1x1)", to indicate that true periodicity is broken by such disorder.

Clarke has studied the room-temperature structure of the clean Mo(100) and of the c(2x2) sulfur overlayer on that surface.[4] He performed a dynamical LEED analysis, which did not allow for lateral displacements in any layer or for interlayer spacing relaxations below the second layer. He determined that the topmost interlayer spacing of the clean Mo(100) surface contracts by about 9.5% from the bulk value. The sulfur atoms in the c(2x2) overlayer were found to adopt the high-symmetry four-fold hollow sites, while the top layer spacing of the Mo crystal reduces its contraction to about 6%. The S-Mo bond length could not be determined in Clarke's analysis. Ion scattering experiments [7] also seem to imply that the sulfur atoms adsorb on the four-fold hollow sites, and indicate that their distance above the Mo top layer is about 1.0Å. Recently, using angle-resolved photoelectron emission fine structure (ARPEFS), Bahr et al [8] have measured a similar S-Mo spacing, and found a Mo interlayer relaxation for the Mo(100)-c(2x2)-S system. All these results seem to indicate that the sulfur atoms reside at the center of high symmetry four-fold hollow sites. However, asymmetrical sites, e.g. sites somewhat displaced from the high-symmetry sites, were not explicitly studied and therefore cannot be ruled out.

In this paper, we report new measurements of LEED intensities, obtained with a video camera, together with a detailed analysis by dynamical calculations for both the clean "(1x1)" and the "c(2x2)" sulfur covered Mo(100) surface. Using R-factor criteria applied to beam I-V curves, multilayer relaxations with parallel displacements in the top layer are found for both of these systems. We shall compare these findings with similar results for W(100)[24] and for O on Ni(100),[25,26] where asymmetrical positions for the surface atoms have also been reported.

2. Experiment

Experiments were performed in an ion pumped stainless steel UHV chamber equipped with a quadrupole mass spectrometer and an ion sputtering gun. The base pressure in our vacuum chamber was around 5×10^{-10} torr.

The Mo(100) sample ($5x7x1mm^3$) was cleaned by standard procedures: heating the sample in 5×10^{-9} torr of O_2 to 900K for about 30sec, pumping the system down to the base pressure,

then flashing the sample to 2000K to remove the oxide.

Sulfur was adsorbed on the Mo surface from an electrochemical cell: Pt/AgI/Ag_2S. When a voltage is applied across the cell, sulfur evolves (in various cluster sizes, but predominantly S_2) and adsorbs on the surface.[27,28] Usually, annealing is required to obtain a sharp LEED pattern. The surface concentration of sulfur and the carbon contamination on Mo were monitored by following Auger emission for the S(152eV), C(272eV) and Mo(221eV) transitions. The carbon contamination was less than 1% by Auger electron spectroscopy.

Several different surface periodicities have been reported for sulfur adsorbed on Mo(100) as a function of sulfur coverage.[6] They are summarized in Table 1. Figure 1 shows the LEED patterns for clean Mo(100)-"(1x1)" and Mo(100)-"c(2x2)"-S. The latter occurs at a coverage of about a half monolayer.

A four-grid LEED optics is used in our experiments. The experimental LEED I-V curves were obtained with a video camera system. The video camera is computer controlled and the diffraction image is recorded on video tape as the incident electron energy is changed. After digitizing the intensity of the diffraction beams in the video image and subtracting the background, the relative intensities of the diffraction beams are obtained. These data are then smoothed, normalized to a constant incident beam current and averaged with other symmetry-equivalent beams, before comparison with theoretical calculations. For the clean Mo(100) surface, I-V curves were measured for the (1,0), (1,1), (2,0), (2,1), (2,2), (3,0) and (3,1) beams over the range 70–300eV at normal incidence. For the Mo(100)-"c(2x2)"-S, I-V curves were measured for ten beams under the same conditions: (1,0), (1,1), (1.5,0.5), (1.5,1.5), (0,2), (2,1), (2.5,0.5), (2.5,1.5), (0,3) and (3,1). No diffuse LEED intensities (due to disorder) were measured or analyzed. Further experimental details are given elsewhere.[29]

3. Theory

The dynamical LEED calculations were based on established methods to produce beam I-V curves.[30,31] For the clean-surface trial structures, renormalized forward scattering (RFS) was used to stack the metal layers. In the Mo(100)-"c(2x2)"-S system the distance between the S and Mo layer could be small due to S penetration into the deep substrate hollows, making the convergence of RFS unreliable. Therefore, the layer doubling method was applied instead.

Lateral shifts in the topmost atomic positions parallel to the surface are possible in these structures. They could be rigid shifts of the entire top layer within a domain (each domain having a shift in a different random direction). Or, more likely, they could be more independent shifts of each atom in more or less random directions by variable amounts. For simplicity, the calculation assumes a single rigid lateral shift of the entire topmost layer, giving strict (1x1) or c(2x2) periodicity. To account for the different equivalent shift directions, the calculated intensities are averaged over the corresponding domains. Thus, we obtain calculated intensities that depend on the shift direction and on the shift amplitude, which are treated as variables to be fitted to experiment. It is known that multiple scattering in LEED is relatively small between atoms in the same layer, especially at our relatively high energies [31,32]. This reduces the error induced by using rigid layer shifts to model random local shifts.

The spherical-wave expansion was cut off at l_{max}=7. Thus, eight phase shifts were used, which were calculated for a cluster of 67 sulfur and molybdenum atoms with approximately the same structure as the expected surface structure.[33] The imaginary part of the muffin-tin potential was held constant at 5eV. The thermal vibration of the surface atoms was included with Debye temperatures of 450K for Mo and 686K for S.

For comparison between experiment and theory, we applied five different R-factors and their average with different weights,[31] as in most of our earlier LEED studies. At that stage

the muffin-tin level is allowed to vary between 5eV and 13eV in 1eV steps.

4. Clean-surface analysis

We started with high-symmetry structures by testing only interlayer spacing variations in the clean surface (model A). The three topmost spacings d_1, d_2 and d_3 were allowed to deviate from the bulk spacing of 1.575Å. The ranges of variation were as follows:

$1.4175 < d_1 < 1.5963$Å in steps of 0.01Å,
$1.5750 < d_2 < 1.6223$Å in steps of 0.01Å,
$1.5435 < d_3 < 1.5908$Å in steps of 0.01Å.

Then, in model B, the top-layer atoms were allowed to vary their position (x,y) in the two dimensions parallel to the surface, in steps of 0.02Å. For each parallel position, the two topmost interlayer spacings were still varied independently during this search (the third spacing remaining fixed at its optimum value from model A).

Table 2 lists the optimum values of these parameters for both models A and B. Figure 2 shows R-factor contour plots for clean Mo(100)-"(1x1)". The minimized values of the five-R-factor average for models A and B are 0.19 and 0.18, respectively, while the corresponding Zanazzi-Jona and Pendry R-factor values are almost indistinguishable: 0.10 and 0.30, respectively, for both A and B. The optimal muffin-tin zero level is found to be 11.5 ± 1 eV below vacuum. Figure 3 illustrates the preferred structural model for Mo(100)-"(1x1)".

5. Sulfur overlayer structure

With the sulfur overlayer, we started with high-symmetry structures (model A), assuming hollow sites. We allowed the two topmost interlayer spacings (S-Mo and Mo-Mo) to vary in the following ranges, with deeper layers taking on bulk spacing values:

$1.0050 < d_1 < 1.0550$Å in steps of 0.01Å,
$1.5050 < d_2 < 1.5750$Å in steps of 0.01Å.

The choice of these ranges was based on the covalent radii of S (1.02Å) and Mo atoms (1.363Å) and the optimal topmost layer spacing for clean Mo(100).

Next, the sulfur atoms were displaced away from the center of hollow sites parallel to the surface (model B) by up to 0.3Å in steps of 0.02Å, in two dimensions. Also, several positions along the line from hollow to bridge site were explored. Again, for each parallel position, the two topmost interlayer spacings were adjusted to minimize the R-factor.

With lateral displacements in a "c(2x2)" overlayer, one may expect concomitant displacements in the layer below it, breaking its (1x1) periodicity; i.e. lateral relaxations could be induced in the metal layer below the sulfur layer. We have, however, not explored such relaxations.

Figure 4 shows R-factor contour plots for Mo(100)-"c(2x2)"-S. The variation in the R-factor with the displacement of the S atoms along the line from hollow sites to bridge sites is shown in Figure 5. It was found that the minimized value of the five R-factor average varies from 0.19 at hollow sites to 0.28 at bridge sites, passing through a minimum of 0.17 at a displacement of 0.20 Å from the center of the hollow sites.

The minimized values of the five-R-factor average for models A and B are 0.19 and 0.17, respectively, while the corresponding Zanazzi-Jona and Pendry R-factor values are 0.14 and 0.40 for A, and 0.12 and 0.36 for B. The optimal structure parameters are listed in Table 3. The optimal muffin-tin zero level is found to be 11 ± 1eV below vacuum.

Figure 6 shows I-V curves for the optimal structure of model B, compared with those of model A and experiment. The structure model itself is presented in Figure 7.

6. Discussion and Conclusions

Our structural result for clean Mo(100) is summarized in Table 4. The multilayer relaxations perpendicular to the surface which we observe in clean Mo(100) are in line with earlier results for bcc(100) surfaces: Table 5 compares those results. For Mo(100) a slight preference emerges for a lateral displacement of the surface atoms by 0.13Å in the <11> surface directions, i.e in the <110> bulk directions, in qualitative agreement with theory.[16] These results should be taken as averages over many possible local configurations. They are quite similar to those for the clean W(100)-"(1x1)" surface. A LEED analysis for clean W indicates a lateral displacement by 0.16Å in the same directions.[24,43] A phenomenological theory applied to W(100)[44] also finds similar displacements.

Our structural result for a half monolayer of sulfur on Mo(100) is presented in Table 6. As expected from numerous previous examples at surfaces,[4,31,34,45] the spacing relaxations of the clean Mo substrate are strongly reduced by the adsorption of sulfur, although a residual contraction of the topmost interlayer spacing remains. This is one more example of the general phenomenon of adsorbate-induced restructuring.[45]

The sulfur adsorption is found to occur near a hollow site. The fit between the theoretical LEED calculations and experiment is clearly improved when allowing a parallel displacement of the sulfur adatoms in the "c(2x2)" structure. The magnitude of the displacement is 0.20Å and it is oriented in the <10> surface directions, i.e. in the <100> bulk directions.

As a result, we find the following Mo-S bond lengths. In the case where the S atoms are restricted to the centers of hollow sites, the S-Mo bond length is 2.46 Å from an S atom to the four Mo atoms in the top metal layer, while it is 2.57 Å to the nearest Mo atom in the second metal layer. After allowing lateral sulfur displacements by 0.20 Å from the center of hollow sites towards the bridge sites, the S-Mo bond lengths involving top-layer Mo atoms are 2.33 Å and 2.58 Å, while the bond length to the second-layer Mo atom is 2.56 Å. Therefore, the S atoms in the optimal structure are bonded most closely to two metal atoms, which reside in the top metal layer, and less closely to three metal atoms, which reside in the first and second metal layers. These bond lengths may be compared with the sum of covalent radii, namely 2.38 Å. The Mo-S bond length in bulk MoS_2 is 2.39 Å; MoS_2 is the most stable compound of sulfur and molybdenum in nature.

Our Mo-S spacing of 1.03 Å may be compared with the 1.005 Å value found with ion scattering for this system,[7] the 0.93 Å value from ARPEFS[8], and the 1.04 Å value from a first-principles total-energy calculation.[46]

Our result for S on Mo(100) is not the first indication of asymmetrical atomic adsorption at surfaces. Recently, scanning tunneling microscopy presented another example where sulfur possibly resides at asymmetrical sites on Mo(100).[10] In the high-coverage (1 monolayer) (2x1) structure, in which severe sulfur crowding occurs, the STM images appear to favor S locations about halfway between hollow and bridge sites in this denser structure. On the other hand, recent calculations of the total energy for S on Mo(100) in the high-coverage (2x1) structure do not favor asymmetrical sites.[46] Asymmetrical sites were not theoretically tested in the c(2x2) structure at a half monolayer coverage, but the hollow site was found to otherwise reproduce several experimental findings, including the Mo-S spacing mentioned above, and the

work function change upon adsorption (0.35 eV vs. 0.4eV from experiment).

Demuth and coworkers obtained a similar lateral adsorbate displacement with an extensive LEED analysis of the structure of Ni(100)-"c(2x2)"-O: here the O atoms were found to reside 0.30Å from the hollow sites in the <10> surface directions, i.e. toward bridge sites.[25] A recent diffuse LEED study of a disordered low-coverage overlayer of O on Ni(100) also revealed possible off-center adsorption, displaced by 0.40Å in the same directions.[26] On the other hand, a very recent LEED study of Ni(100)-c(2x2)-O suggests that buckling of the second Ni layer can remove the need for asymmetrical sites.[47]

It appears that lower-symmetry adsorption is a strong possibility in many adsorption systems. Relatively little effort has gone into proving or disproving the existence of asymmetrical adsorption in the past. Most structural determinations have assumed high-symmetry adsorption sites, and it is quite possible that asymmetrical distortions from those sites would improve the fit to experiment in certain cases.

An issue not addressed in this study is the possibility of adsorbate-induced lateral relaxations in the metal positions. In view of the clean-surface reconstruction (disordered at room temperature), this is a strong possibility which is at present under investigation. Also being explored is the possibility of a buckling in the second metal layer, as well as issues of accuracy. Preliminary results support our finding of asymmetrical sites and insignificant buckling in the second metal layer.[48]

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Table 1. Surface periodicities for S on Mo(100), as a function of sulfur coverage

Coverage range (monolayers)	LEED patterns
0.0–0.3	(1x1)
0.3–0.5	c(2x2)
0.65–0.7	$\begin{pmatrix} 2 & -1 \\ 1 & 1 \end{pmatrix}$
0.75–0.9	c(4x2)
0.9–1.1	p(2x1)

Table 2. Optimal structural parameters for the clean Mo(100)-"(1x1)" surface; (d_x, d_y) represents a displacement of a topmost atom parallel to the surface, relative to the ideal bulk position and in terms of the (x, y) coordinates in the square surface unit cell; the first, second and third spacings are denoted d_1, d_2 and d_3, respectively (all distances in Ångstrom units); the bulk interlayer spacing is 1.575Å.

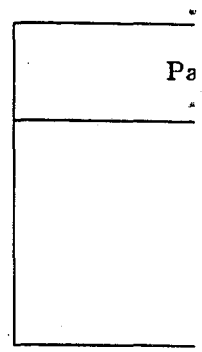


Table 3. Optimal structural parameters for the Mo(100)-"c(2x2)"-S surface (notation as in Table 2).

Parameter	Model A	Model B
d_x	0.00	0.20±0.05
d_y	0.00	0.00
d_1	1.04±0.02	1.03±0.02
d_2	1.54±0.03	1.53±0.03

Table 4: Structural result for Mo(100)-"(1x1)" in the format of the Surface Crystallographic Information Service (SCIS) handbook [34]

SURFACE:

Substrate: Mo
Bulk structure: bcc
Adsorbate: –
Adsorbate state: –

Face: (100)
Temperature: 300K
Surface pattern: disordered (1x1)
Coverage: –

STRUCTURE:

Reference unit cell: a=3.1468Å, b=3.1468Å, A(a,b)=90°
2D symmetry: pm
Thermal vibrations: θ_D=318K
R-factors: R_{VHT}=0.18, R_{ZJ}=0.10, R_{PE}=0.30

Layer	Atom	Atom positions	Normal layer spacing	Error
S1	Mo	0.03 0.03	1.49	0.02
S2	Mo	0.5 0.5	1.60	0.02
S3	Mo	0.0 0.0	1.58	0.02
S4	Mo	0.5 0.5	1.575	–

Table 5: Percentage interlayer spacing relaxations for clean bcc(100) surfaces, from LEED; the first, second and third spacing changes are denoted Δd_1, Δd_2 and Δd_3, respectively.

Element	Δd_1	Δd_2	Δd_3	Reference
Fe	-1.4±3 -5±2	 +5±2		[35] [36]
Mo	-9.5±2 -6±1.5	 +2±2	 +0.5±3	[4] this work
Ta	-11	+1		[37]
V	-7 -6.7±1.5	+1 +1.0±1.3		[38] [39]
W (1x1)	-8±1.5 -7±1.5 -6.5±6.5			[40] [41] [42]
W c(2x2)	-7±2	+1.3±2		[43]
W "(1x1)"	-8			[24]

Table 6: Structural result for Mo(100)-"c(2x2)"-S in the format of the Surface Crystallographic Information Service (SCIS) handbook [34]

SURFACE:

Substrate: Mo	Face: (100)
Bulk structure: bcc	Temperature: 300K
Adsorbate: S	Surface pattern: disordered c(2x2)
Adsorbate state: atomic	Coverage: 0.5(S/Mo)

STRUCTURE:

Reference unit cell: a=4.4502Å, b=4.4502Å, A(a,b)=90°
2D symmetry: pm
Thermal vibrations: θ_D=318K(Mo), 485K(S)
R-factors: R_{VHT}=0.18, R_{ZJ}=0.12, R_{PE}=0.36

Layer	Atom	Atom positions	Normal layer spacing	Error
A1	S	0.032 0.032	1.03	0.02
S1	Mo	0.5 0.0	0.0	–
S2	Mo	0.0 0.5	1.53	0.03
S3	Mo	0.0 0.0	0.0	–
S4	Mo	0.5 0.5	1.575	–

Figure captions

Figure 1. Photographs of the LEED patterns of (a) the clean Mo(100) crystal surface; and (b) the sulfur "c(2x2)" overlayer on Mo(100). The incident electron energies are 84eV and 91eV, respectively. Normal incidence is used.

Figure 2. R-factor contour plots for clean Mo(100): (a) model A with only multilayer relaxations (d_1, d_2); and (b) model B with in addition lateral displacements (d_x, d_y) in the topmost layer, for the best interlayer spacings.

Figure 3. Plan view of our structure model for Mo(100)-"(1x1)": at left without lateral displacements, at right assuming randomly oriented displaced surface atoms. Displacements are drawn to scale, but arrows are not.

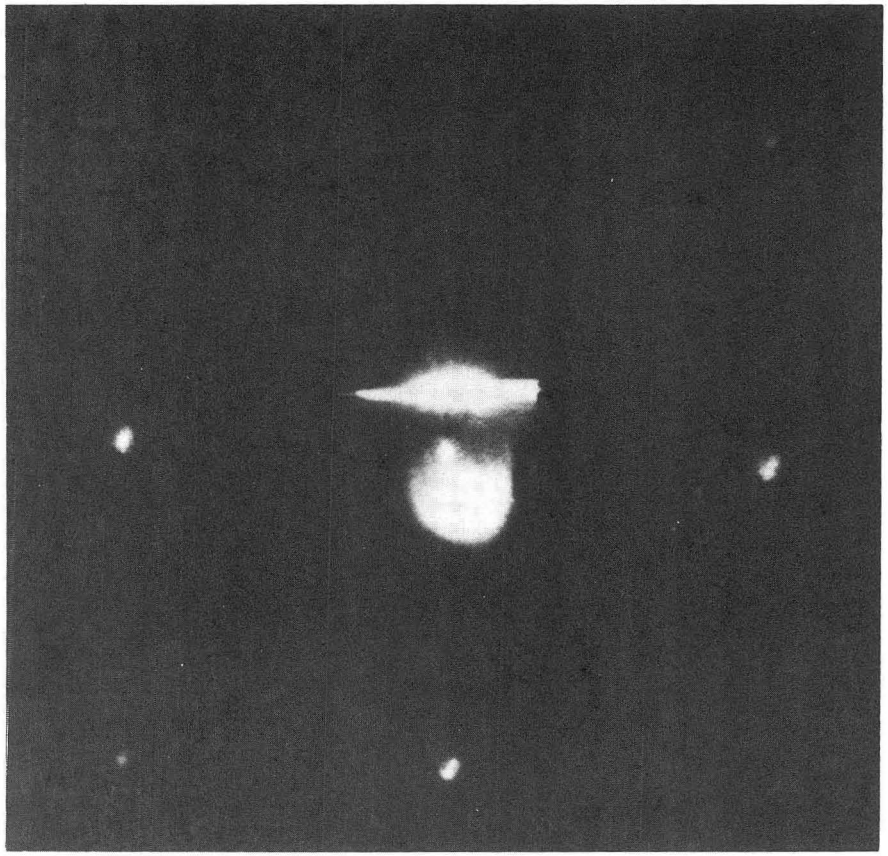
Figure 4. R-factor contour plots for Mo(100)-"c(2x2)"-S: (a) model A with only multilayer relaxations (d_1, d_2); and (b) model B with in addition lateral displacement d_x of the sulfur layer, assuming a bulk-like d_2 (which is not the optimum d_2).

Figure 5. Variation of the R-factor for Mo(100)-"c(2x2)"-S with the S-atom displacement along the <10> directions, from hollow site ($d_x = 0$) to bridge site (d_x =1.575Å) .

Figure 6. Representative calculated I-V curves for Mo(100)-"c(2x2)"-S for the optimal structures in models A (spacing relaxations only) and B (lateral displacements also), compared with the experimental measurements. Note the variable energy ranges and scales, and the vertical offsets between curves (baselines are marked by ticks).

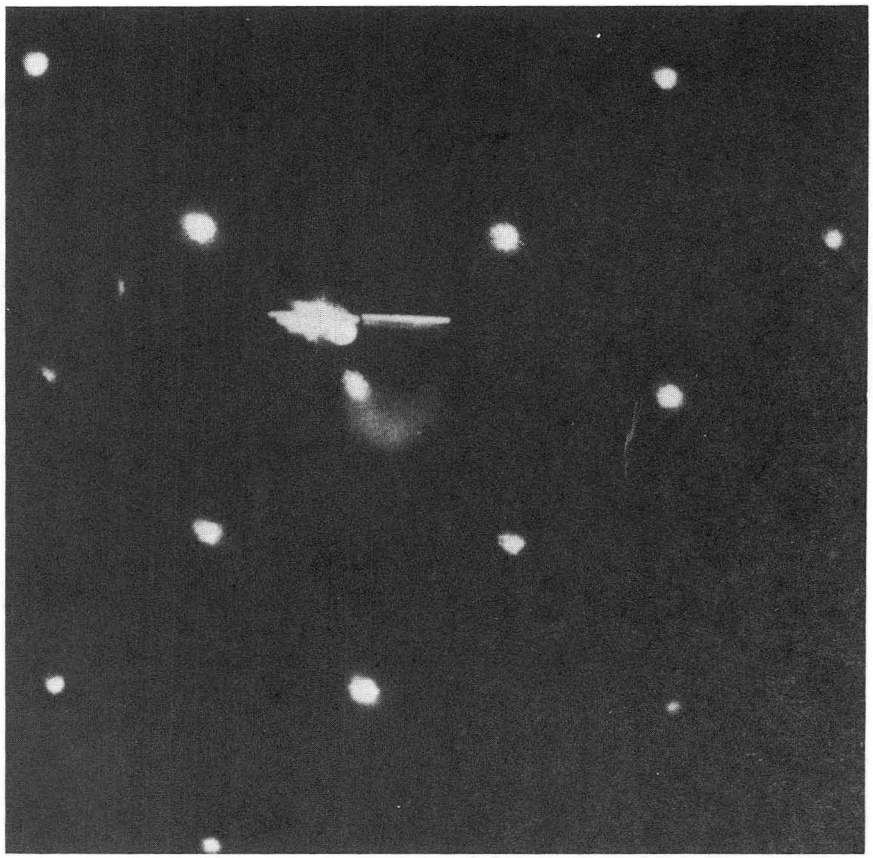
Figure 7. Plan view of our structure model for Mo(100)-"c(2x2)"-S: at left without lateral displacements, at right assuming randomly oriented displaced sulfur atoms (shown as smaller circles). Displacements are drawn to scale, but arrows are not.

LEED patterns



a

Mo(100)–(1×1)

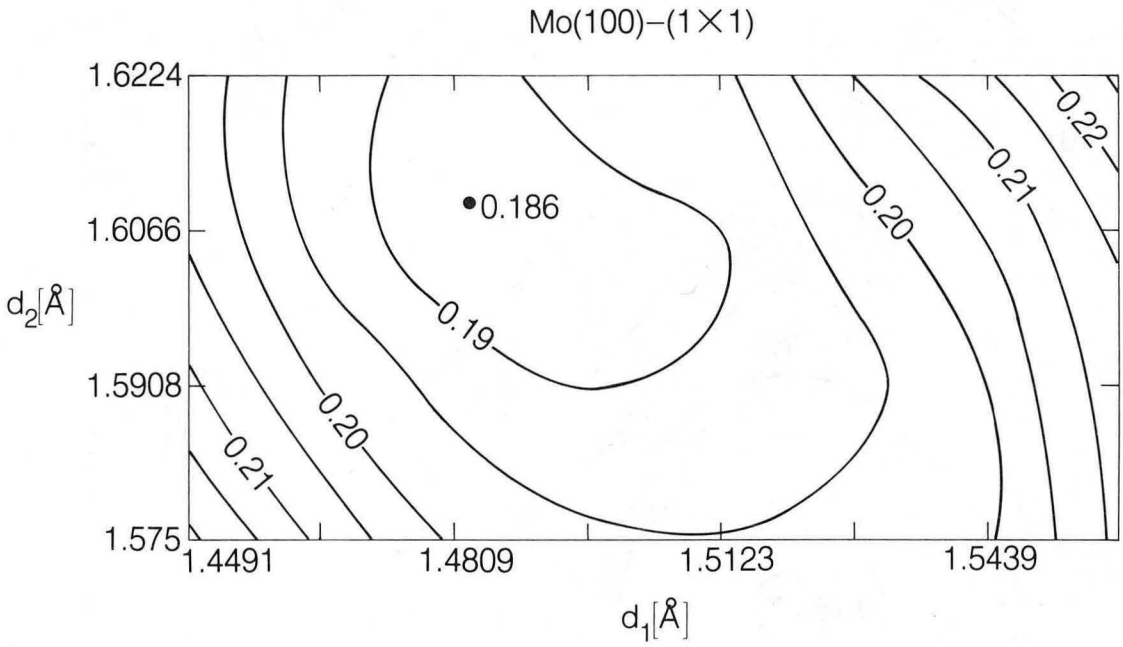


XBB 880-11272

b

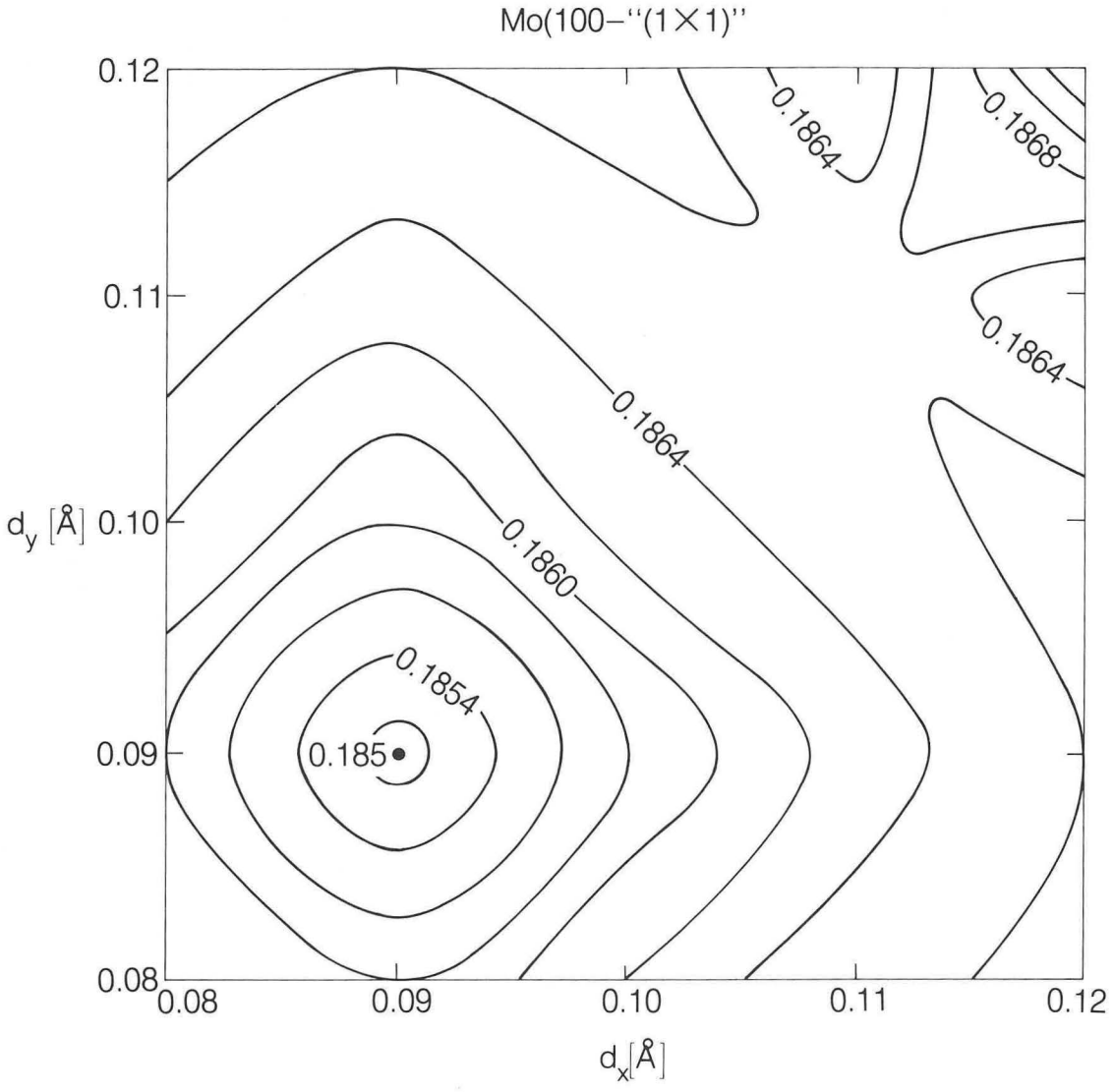
Mo(100)–c(2×2)–S

Fig. 1



XBL 8811-8613

Fig. 2a



XBL 8811-8612

Fig. 2b

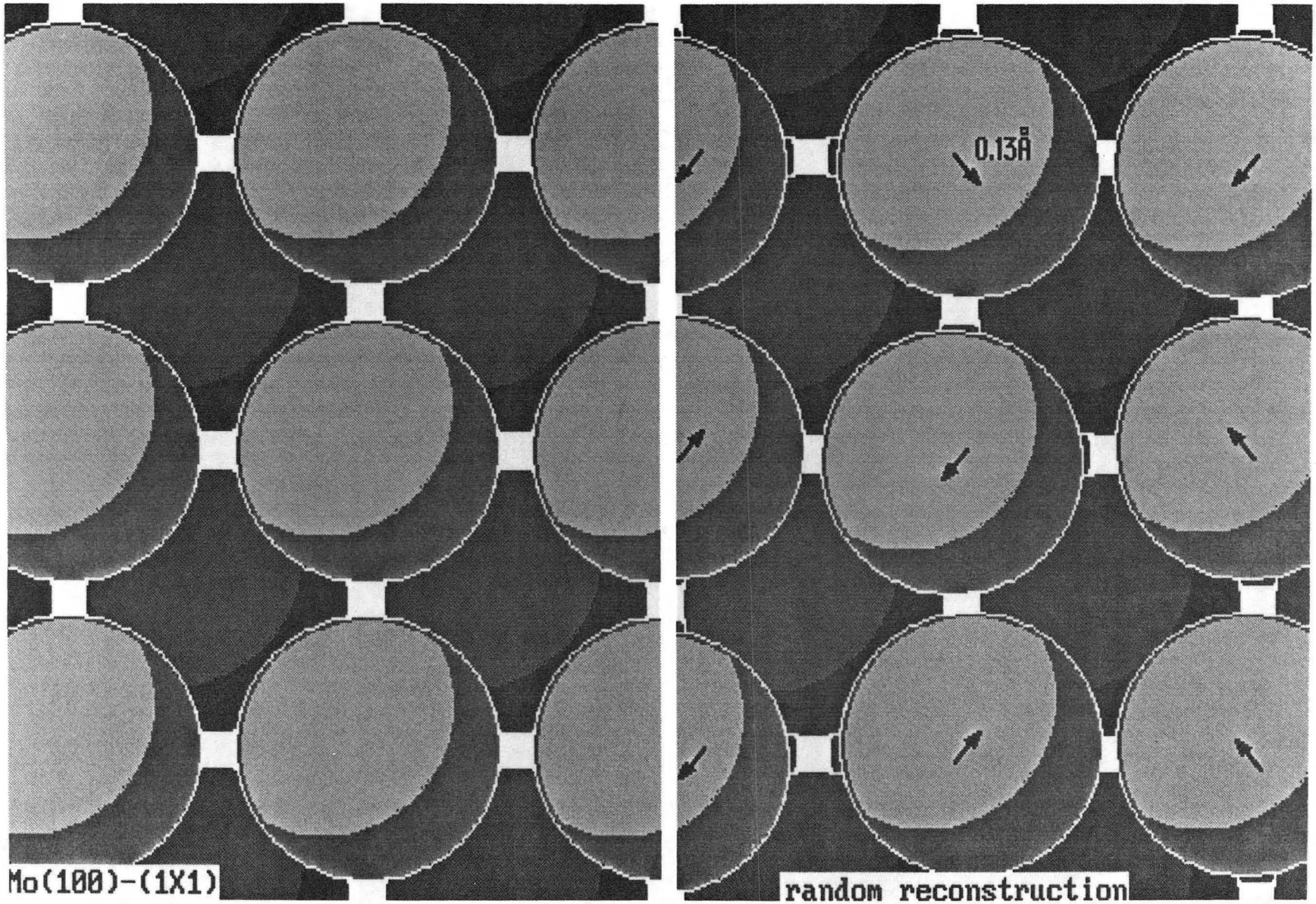
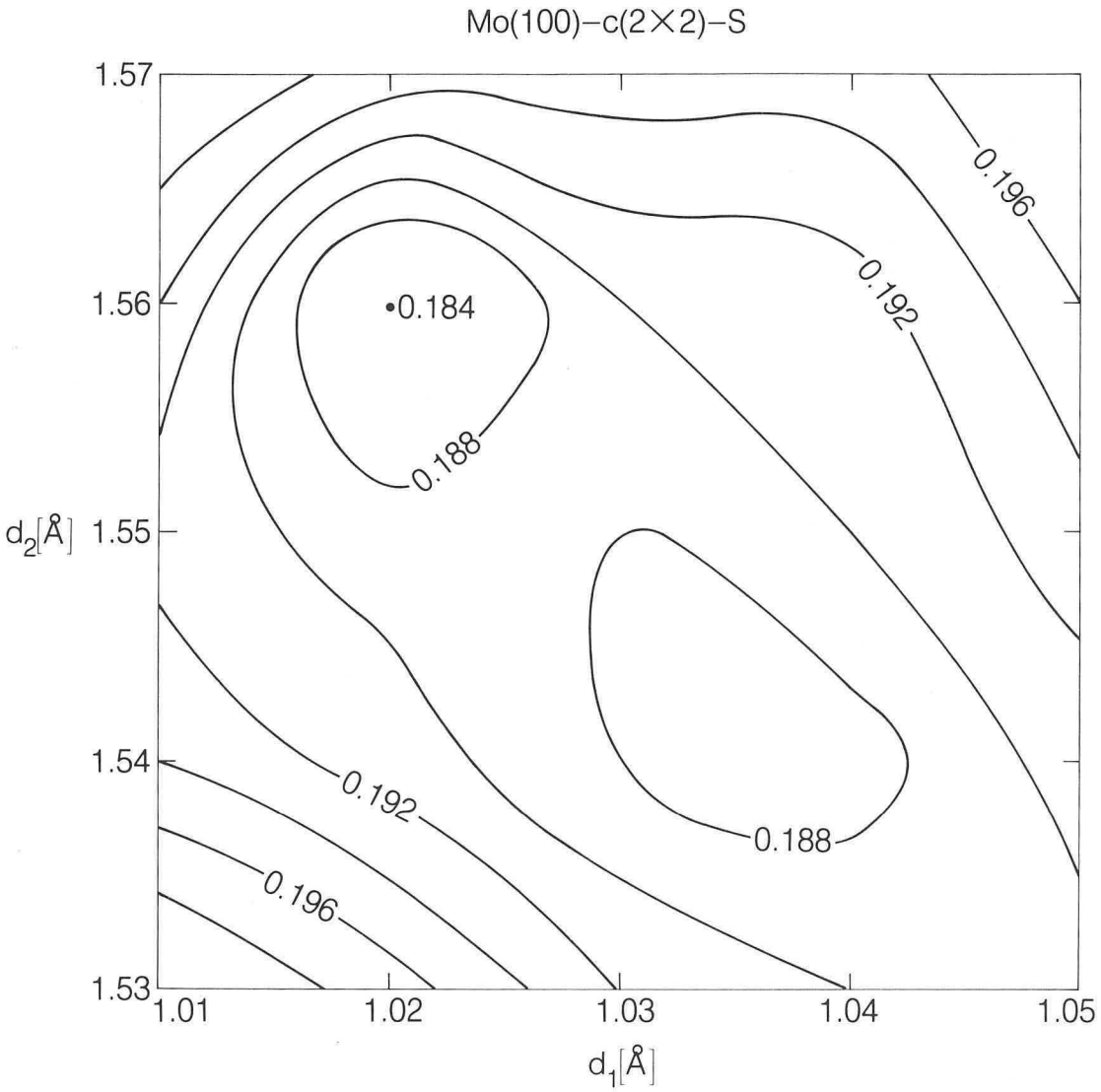


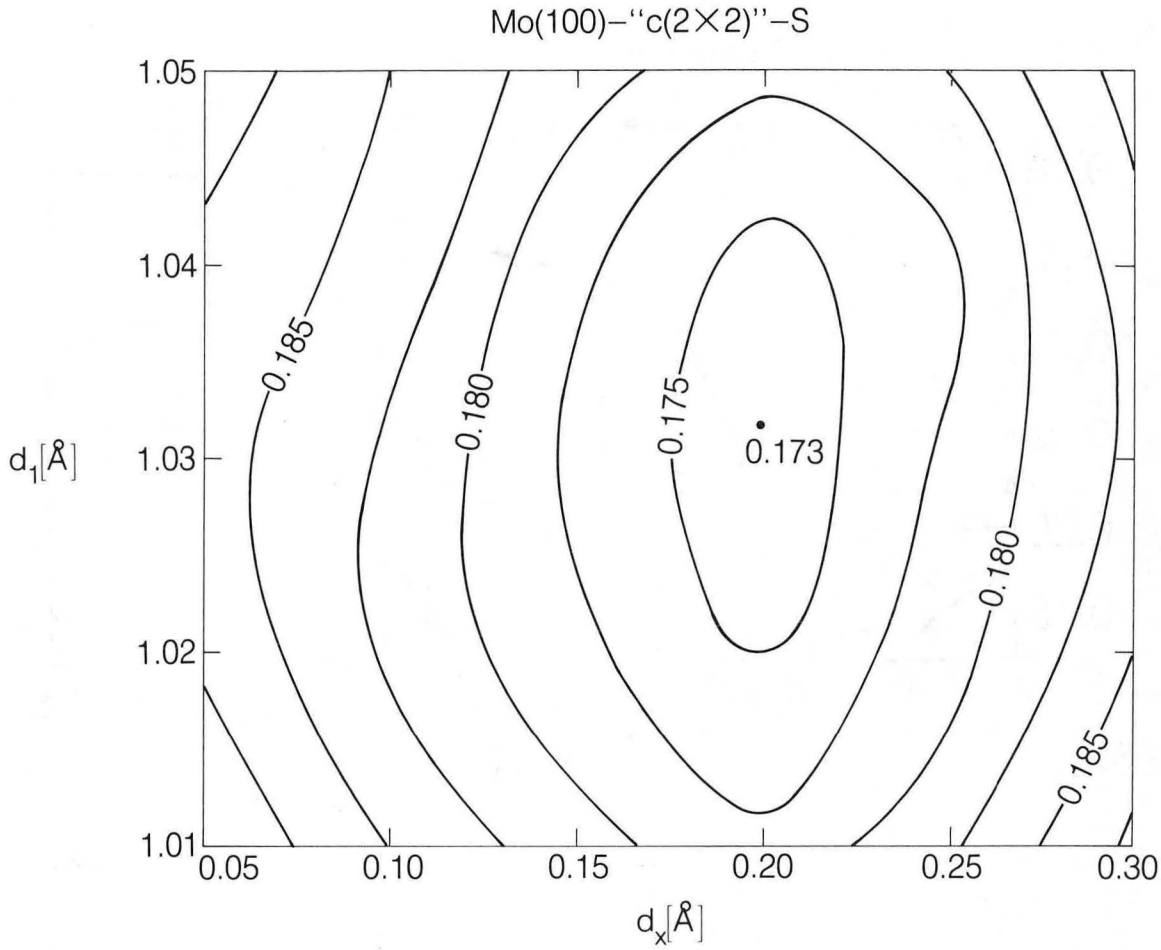
Fig. 3

XBB 880-11273



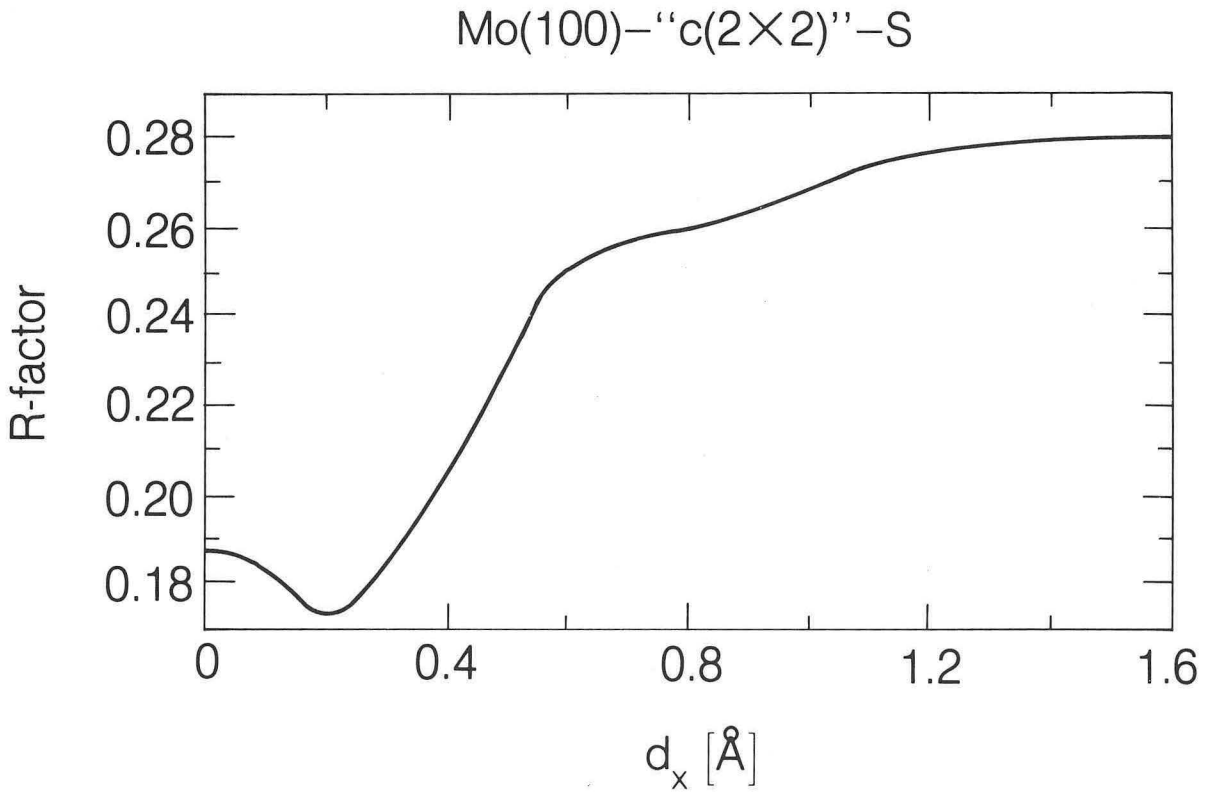
XBL 8811-8614

Fig. 4a



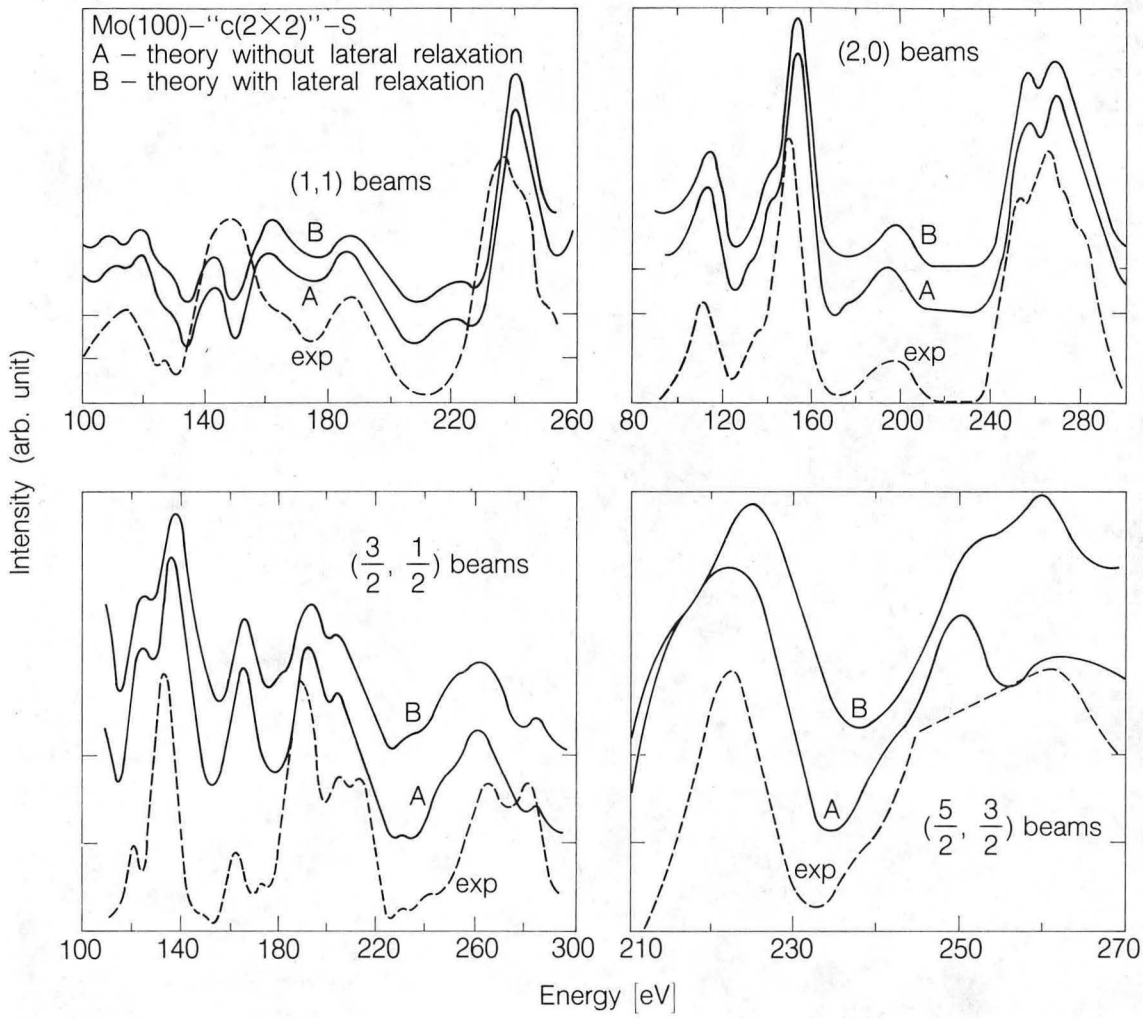
XBL 8811-8617

Fig. 4b



XBL 8811-8615

Fig. 5



XBL 8811-8616

Fig. 6

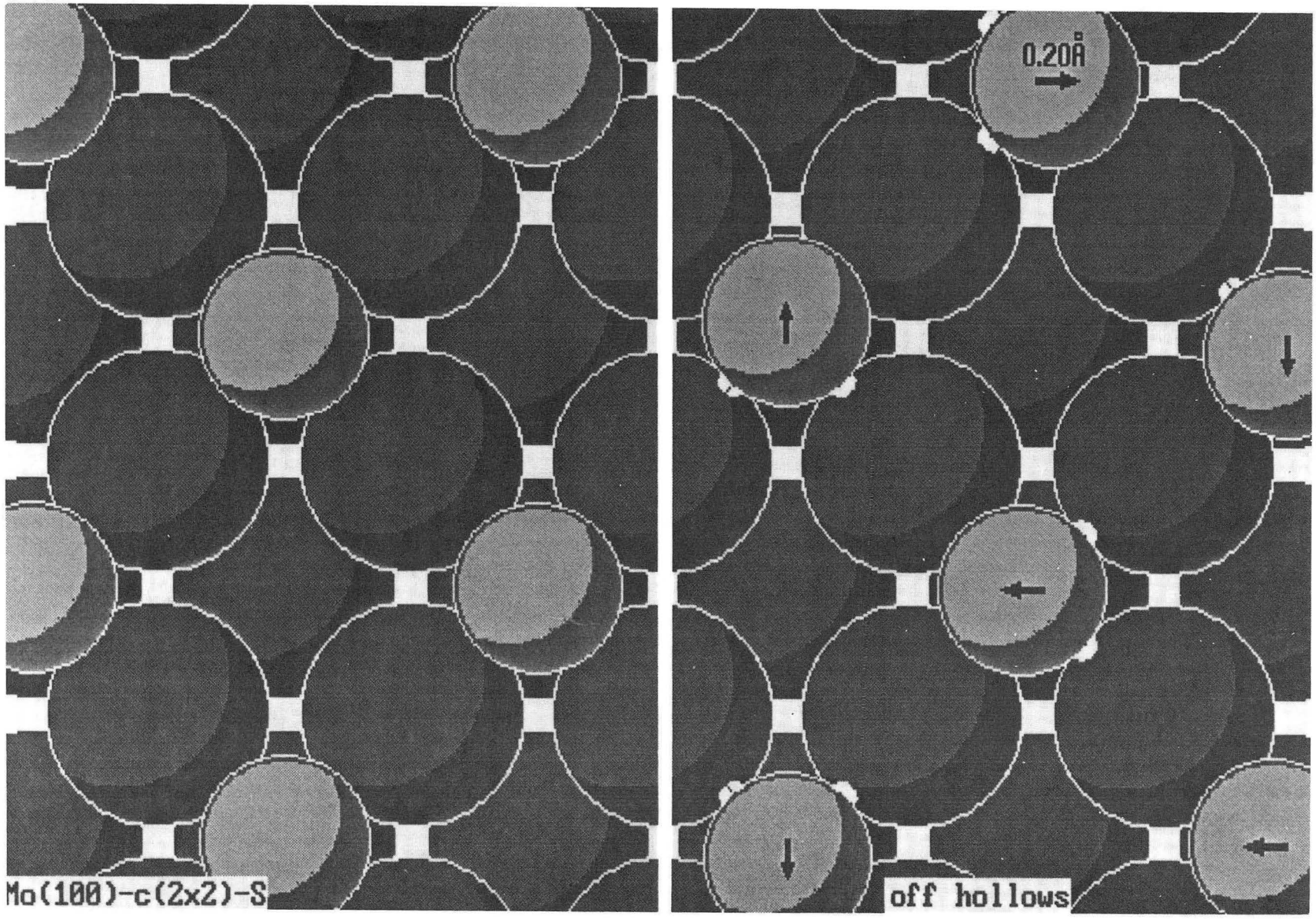


Fig. 7

XBB 880-11274

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