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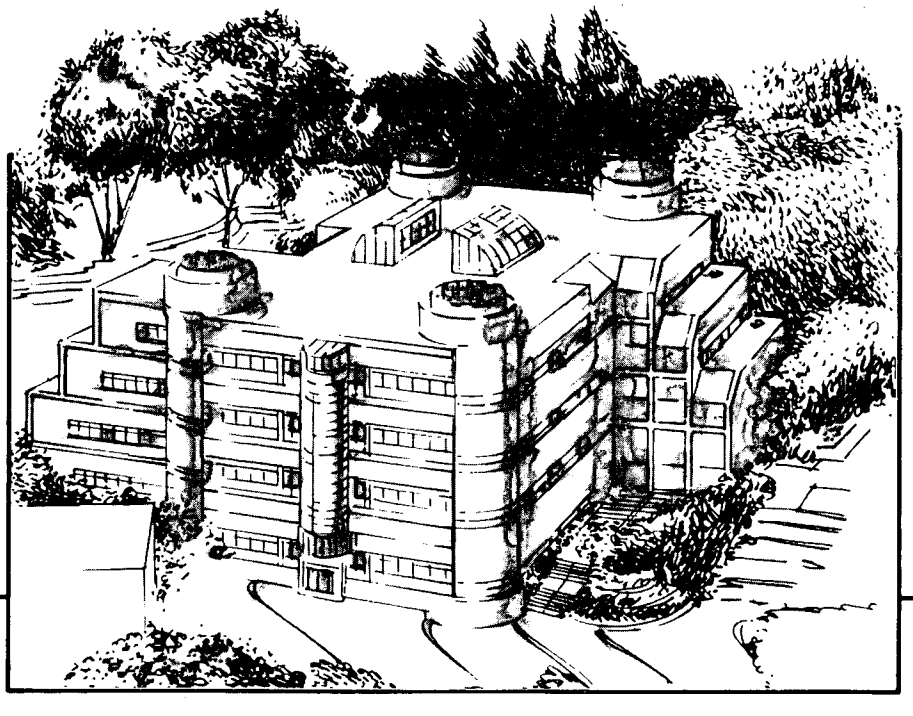

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ABSTRACT

The structure of sulfur adsorbed on the basal plane of rhenium has been studied in UHV with Auger, LEED and STM. At low coverages ($<$ 0.25 monolayers) single sulfur adatoms form open structures with p(2x2) and c($\sqrt{3}$x5) *rect* lattices. In these structures both the sulfur adatoms and some of the rhenium substrate atoms are imaged simultaneously, identifying the sulfur adsorption site as a three fold hollow site. At coverages above 0.25 ML sulfur adatoms aggregate into trimers, first disordered and then ordered into a ($3\sqrt{3}$x$3\sqrt{3}$)R30° lattice at a coverage of 0.45 ML. Two types of trimers form that are centered around different substrate sites. Between 0.45 and 0.5 ML diamond-shaped sulfur tetramers appear until an ordered $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ structure forms. With further exposure to H_2S a final structure is formed, consisting of hexagonal sulfur rings in a ($2\sqrt{3}$x$2\sqrt{3}$)R30° lattice. All of the sulfur adatoms in the three high coverage structures occupy the same type of three fold hollow sites as in the low coverage structures.

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1. INTRODUCTION

Sulfur chemisorption on metal surfaces has been studied extensively over the past years.[1,2,3] At low coverages adsorbed sulfur atoms form open lattices -- c(2x2) on the (100) surfaces of bcc and fcc metals and p(2x2) or $(\sqrt{3}x\sqrt{3})R30^\circ$ on the (111) and (0001) surfaces of fcc and hcp metals.[4,5] The sulfur binding energy is quite high at low coverages and decreases for coverages above 0.25 ML (monolayer, defined as one sulfur adatom per substrate unit cell) or 0.33 ML as the sulfur adatom spacing is reduced. For example, on Pt(111), sulfur in the $(\sqrt{3}x\sqrt{3})R30^\circ$ structure does not desorb until the temperature is above 1300 K, while at higher coverages (above 0.33 ML) sulfur first desorbs at 800 K.[6] Similarly, on Re(0001) the low coverage 0.25 ML structure desorption peak occurs at 1600 K, while at 0.5 ML the sulfur desorption peaks at 900 K.[17] The decrease of binding energy when the coverage increases above 0.25 or 0.33 ML is a result of the large repulsive interactions between sulfur adatoms in near neighbor positions.

Sulfur adsorbed on Re(0001) is particularly interesting from the structural point of view. With low energy electron diffraction (LEED), four ordered structures have been observed as a function of sulfur coverage.[1] A primitive p(2x2) LEED pattern is observed when the coverage range is between 0.16 and 0.30 ML, according to an Auger (AES) calibration. Between 0.30 and 0.39 ML a $(3\sqrt{3}x3\sqrt{3})R30^\circ$ lattice is observed. At this coverage the surface is inert to CO and

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small hydrocarbon adsorption in vacuum. Two more structures are formed near saturation coverage, the $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ when the coverage is between 0.39 and 0.44 ML and the $(2\sqrt{3}x2\sqrt{3})R30^\circ$ between 0.44 and 0.59 ML monolayers.[1]

The structures of low coverage sulfur lattices have been determined by LEED for several metal surfaces. In all cases the sulfur adatoms were found to adsorb on top of the first metal layer in the site with the highest available coordination number -- three fold sites on (111) and (0001) surfaces and four fold sites on (100) surfaces.[5] No LEED structure calculations have been completed for higher coverage sulfur structures with more than one adatom per unit cell, although such calculations are in progress for sulfur on Re(0001).[8] The Re(0001) sulfur structures are quite difficult to analyze, with 12 rhenium and 6 sulfur atoms in the in the surface unit cell for the $(2\sqrt{3}x2\sqrt{3})R30^\circ$ lattice, 8 rhenium and 4 sulfur atoms for the $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ lattice and 27 rhenium and 12 sulfur atoms for the $(3\sqrt{3}x3\sqrt{3})R30^\circ$ lattice. The combination of STM and LEED may prove to be the only practical way to analyze such complex structures. This paper presents the results of a recent STM study that analyzes the above structures. Some of the results obtained were unexpected, like the clustering of sulfur adatoms into trimers when the coverage exceeds 0.25 ML.[9] The STM images also show a variety multitude of defects that cannot be studied with LEED and a new structure that has not been detected by LEED.

2. EXPERIMENTAL

The STM measurements were performed in an ultra-high vacuum (UHV) chamber with a background pressure in the 10^{-10} torr range. The chamber was equipped with a LEED optics, a cylindrical mirror analyzer for Auger spectroscopy and a quadrupole mass spectrometer. The STM, electronics and computer software were designed and built in our laboratory.[10]

The single crystal Re(0001) sample was mounted on a tantalum sample holder and placed on a manipulator equipped with an electron beam heater. The Re sample was cleaned by heating in O_2 to remove carbon contamination as measured by AES. Sulfur was adsorbed by heating the sample to 850 K and exposing it to H_2S gas at or below 10^{-7} torr until the desired sulfur coverage was obtained. The crystal was moved to the LEED instrument to confirm the desired lattice was present, and then placed in contact with a copper block cooled by liquid nitrogen. Once the

sample holder cooled to room temperature it was placed in the STM and brought within piezo range of the STM tip. The elapsed time between initial sample preparation and the start of STM imaging was around one hour.

Tunneling tips were formed by mechanically cutting 1 mm diameter Pt-40% Rh alloy wire. STM images were obtained both in topographic (constant current) and current (constant height) modes with gap resistances between 20 and 200 MΩ. There was no significant change in image contrast for bias voltage between -1.5 and +1.5 volts. The gap became less stable and the image quality deteriorated for bias voltages outside this range. Tip velocity during image acquisition was typically 100 to 2,000 Å/s for topographic images and 2,000 to 7,000 Å/s for current images.

3. STM RESULTS

3.1. Low Coverage

At a sulfur coverage of approximately 0.25 ML the p(2x2) is the dominant structure. The STM images show well ordered spots in topographic and in current imaging modes. Ordered p(2x2) regions have been observed adjacent to ordered regions of small sulfur aggregates with higher local coverage, as shown in figure 1a. This image includes an anti-phase domain boundary where two p(2x2) areas are shifted by half the unit cell size, i.e. the Re-Re lattice spacing.

Small domains of a new sulfur structure with a c($\sqrt{3}$x5) *rect* lattice (or $\begin{pmatrix} 2 & 1 \\ 1 & 3 \end{pmatrix}$ in matrix notation) and a local coverage of 0.20 ML were observed (figure 2a). The sulfur adatoms appear as large elongated balls, arranged in rows and separated by $\sqrt{3}$ times the Re-Re lattice spacing or 4.75 Å. The parallel sulfur rows are separated by 6.85 Å (figure 2b). LEED observations of this low coverage structure have never been reported. This may be because the structure is metastable, like the 5x5 or 9x9 reconstructions on Si(111), or because of CO coadsorption. We have observed that the p(2x2) structure is disordered by CO coadsorption, and the more open .20 ML structure may be even more sensitive.

Close examination of the p(2x2) and c($\sqrt{3}$x5) *rect* STM topographs shows small protrusions located between the sulfur adatoms. We believe that these protrusions correspond to those rhenium substrate atoms that do not form Re-S bonds. There are two such protrusions per unit

cell in the c($\sqrt{3}$x5) *rect* lattice, arranged in a zig-zag pattern between the rows of sulfur atoms and one protrusion per unit cell in the p(2x2) lattice. This interpretation requires that sulfur adatoms must sit in a three-fold hollow sites (figure 1a and 2a). We cannot distinguish between the two non-equivalent hollow sites, the hcp hollow site (directly above a second layer Re atom) and the fcc hollow site (with no Re atom in the second layer). Low coverage adsorption in hollow sites on Re(0001) is consistent with the results of LEED structure calculations for ($\sqrt{3}$x$\sqrt{3}$)R30° sulfur lattices on Ir(111), Pt(111), Pd(111) and Rh(111).[5]

The rhenium atom protrusions are rarely observed in current images and not always observed in topographs. Optimal tip structure is required to obtain the necessary high resolution. What may be needed is a tip with one single atom protruding from the apex. This is due to the small distance of 3.2 Å between the sulfur and the Re atoms in the image (projected in the surface plane). Another requirement is that the tip has to be able to come close to the surface, penetrating between the sulfur atoms. In current images the tip does not dip down between adatoms, so the substrate atoms are usually not resolved. In the higher coverage structures all the surface metal atoms participate in S-Re bonds (except for 1 of 27 in the (3$\sqrt{3}$x3$\sqrt{3}$)R30° structure) and we observed no substrate protrusions.

The value of the topographic corrugation of the sulfur structure is larger than expected. Values between 0.3 and 3.0 Å have been observed at a variety of bias voltages and in both polarities. We believe that these values do not reflect the true topographic corrugation of the surface electronic structure but contain contributions from elastic deformations of the tip-surface system.[11] The apparent shape of the sulfur atoms shows variations that may also be related to tip-surface forces and tip condition. In some images the atoms look like triangles while in others they look like balls. The triangles can grow together and create an overall impression of a honeycomb lattice.

3.2. High Coverage Structures

As more sulfur is deposited on the surface, a dramatic change in the sulfur adatom arrangement takes place. Instead of forming the next ordered single atom structure, namely the ($\sqrt{3}$x$\sqrt{3}$)R30° with a local coverage of 0.33 ML, sulfur coalesces into trimers found within p(2x2) regions, as shown in figure 3. Initially almost all the trimers are oriented in the same

direction, often clustering around domain boundaries of the p(2x2) regions. By carefully comparing the registry of the trimers with the adatoms in the p(2x2) lattice we know that the sulfur-sulfur distances within a trimer equal the rhenium lattice spacing or 2.7 Å and that each trimer sulfur atom must sit in the same type of three-fold adsorption sites as the sulfur atoms in the p(2x2) structure.

The interaction responsible for sulfur aggregation is mediated by the substrate. It indicates that the formation of trimers is energetically more favorable than a $(\sqrt{3}x\sqrt{3})R30^\circ$ structure where the adatoms are sitting in hollow sites separated by $\sqrt{3}$ times the Re-Re lattice spacing. Sulfur adsorbed on several other (111) or (0001) metal surfaces does show a p(2x2) to $(\sqrt{3}x\sqrt{3})R30^\circ$ transition. Three adatom interactions are usually considered to be corrections to the normal pairwise interactions typically used in Monte Carlo calculations of lattice gas models.[12,13] In the present system, three or more adatom interactions dominate the pair-wise repulsions and determine the structure of the sulfur overlayer between 0.25 and 0.5 monolayers. This is, to our knowledge, the clearest example of the importance of three adatom interactions in adsorbate surface ordering.[9]

As the sulfur coverage increases, the density of trimers increases until a coverage of 0.45 ML is reached. The trimers then form an ordered $(3\sqrt{3}x3\sqrt{3})R30^\circ$ structure as shown in figure 4a. It is interesting to notice that there are two types of trimers in this structure rotated 60° from each other. These correspond to trimers that are centered around a hollow site of the Re(0001) substrate ("hollow site trimers") or around a top site ("top site trimers") as shown in figure 4b. When trimers are formed within the p(2x2) structure they are almost exclusively "hollow site trimers", indicating that they are energetically more stable. The "top site trimers" form only towards the high end of the 0.25 to 0.45 ML coverage range. Hollow site trimers outnumber top site trimers three to one in the ordered $(3\sqrt{3}x3\sqrt{3})R30^\circ$ structure. Top and hollow site trimers form ordered sublattices, with the top site trimers alternating with hollow site trimers every second row. Figure 4 also shows a domain boundary between two trimer regions where sulfur monomers alternate with diamond shaped tetramers.

Another sulfur aggregate structure is observed at a coverage of 0.5 ML where the surface is covered with diamond shaped sulfur tetramers. These can coexist with the lower coverage structures but become dominant at coverages above 0.45 ML. At saturation the tetramers form an

ordered $\begin{pmatrix}3 & 1\\ 1 & 3\end{pmatrix}$ lattice as shown in figure 5. A close look at the tetramers indicate that there is only one symmetry plane, along the long diagonal. One "end" atom appears brighter than the "side" atoms and the other end atom in both topographic and current images. It is not clear at present whether this is a real height difference or a reflection of the electronic structure of the cluster. No change in contrast was observed as the bias voltage was swept between -1.0 and +1.0 volts.

By examining the configuration of both the trimer and tetramer structures it is easy to see that only local displacements of sulfur adatoms are required to convert trimers into tetramers. This may explain the coexistence of the two structures at intermediate coverages. Previous models proposed for this structure failed to predict the observed clustering of sulfur, due in part to errors in estimating the local coverage from Auger peak heights. The present study shows unambiguously that at saturation the local coverage in the $\begin{pmatrix}3 & 1\\ 1 & 3\end{pmatrix}$ lattice is exactly 0.5 monolayers. It is surprising that the next structure observed by LEED and also in a previous STM study,[2] namely the $(2\sqrt{3}x2\sqrt{3})R30°$, has the same 0.5 ML coverage. The STM images from this last "saturation" structure show that it is made up of repeating sulfur hexagons. The $(2\sqrt{3}x2\sqrt{3})R30°$ structure is produced by high exposures to either H_2S or S_2 gases.[1]

Heating a rhenium crystal with an ordered $(2\sqrt{3}x2\sqrt{3})R30°$ structure in vacuum produces all the other LEED patterns as sulfur is progressively desorbed from the surface. The thermodynamics of the two 0.5 monolayer structures is not understood at present. It may be that the $\begin{pmatrix}3 & 1\\ 1 & 3\end{pmatrix}$ structure is more stable at coverages below 0.5 ML since tetramers are easily converted into trimers at intermediate coverages, while the local coverage of the $(2\sqrt{3}x2\sqrt{3})R30°$ structure cannot be reduced without completely disrupting the hexagon pattern.

4. CONCLUSION

We have observed a new phase for adsorbate atoms that has not been seen previously. This phase results from the formation of small, isolated aggregates under the influence of operation of strong three and more adatom interactions. Our present results are a clear demonstration of the power of the STM technique for investigating chemisorption systems. Except for the low coverage structures with one adsorbate atom per unit cell, the structures found in this study would be difficult to analyze using diffraction methods alone. This is particularly true for the partly

ordered intermediate coverages above 0.25 ML.

Acknowledgements

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FIGURE CAPTIONS

1a A 50 Å square topographic image of the p(2x2) structure acquired at 0.5 nA with a sample bias of -290 mV. The total Z range is 4.9 Å. Out of phase p(2x2) domains are visible at the top and left of the image and a $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ domain occupies the lower right corner of the image. (These images have not be corrected for thermal drift or piezo non-orthogonality.)

1b A schematic diagram of the p(2x2) structure showing sulfur adatoms on the Re(0001) substrate. The hatched circle indicates the sulfur Van der Waal radius of 1.80 Å and the smaller solid ring shows the 0.9 Å covalent radius of sulfur adsorbed on a metal surface.

2a A 24 Å square topographic image of the c($\sqrt{3}$x5) *rect* structure acquired at 0.5 nA with a sample bias of -210 mV. The Z range is 4.1 Å. A sulfur adatom in the upper left corner of the image is displaced from its normal position in the c($\sqrt{3}$x5) *rect* lattice into an interstitial position. The zig-zag pattern between the adatom rows corresponds to the positions of the rhenium substrate atoms.

2b A schematic diagram of the c($\sqrt{3}$x5) *rect* lattice showing sulfur adatoms and rhenium substrate atoms on Re(0001).

3 A 40 Å square current image of the p(2x2) overlayer with included trimers. Sample bias -10 mV and average current 2 nA.The total current range is 3.8 nA. In this image the sulfur atoms in the p(2x2) lattice appear triangular. The included trimers are the larger, brighter triangles. Note the common orientation of the trimers.

4a A 100 Å square topographic image of the ($3\sqrt{3}$x$3\sqrt{3}$)R30° lattice acquired at -50 mV sample bias and 2.2 nA tunnel current. The Z range is 2.0 Å. Note the two non-equivalent trimer orientations. There is an anti-phase boundary between one domain in the upper half of the image and another in the lower left corner of the image.The misfit at the domain boundary is taken up by alternating sulfur tetramers and monomers which appear as "rosette" clusters.

4b A schematic diagram of the $(3\sqrt{3}x3\sqrt{3})R30.^{\circ}$ lattice.

5a A 68 Å square current image of the ordered $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ lattice. The sample bias was -35 mV, the average tip current was 3 nA and the total current range was 6.7 nA. Note the asymmetry of the sulfur tetramers. The sulfur atom at the upper left end of the tetramer appears brighter than the others.

5b A schematic diagram of the $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ lattice.

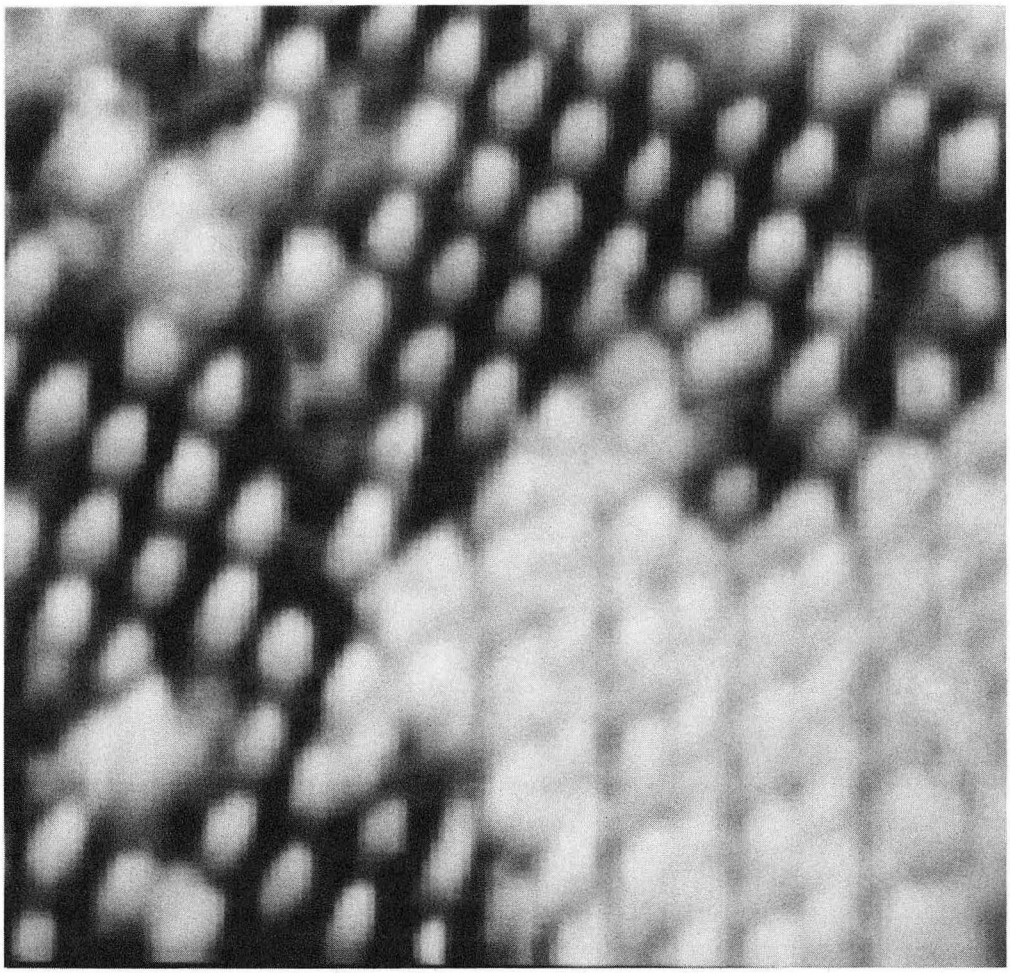

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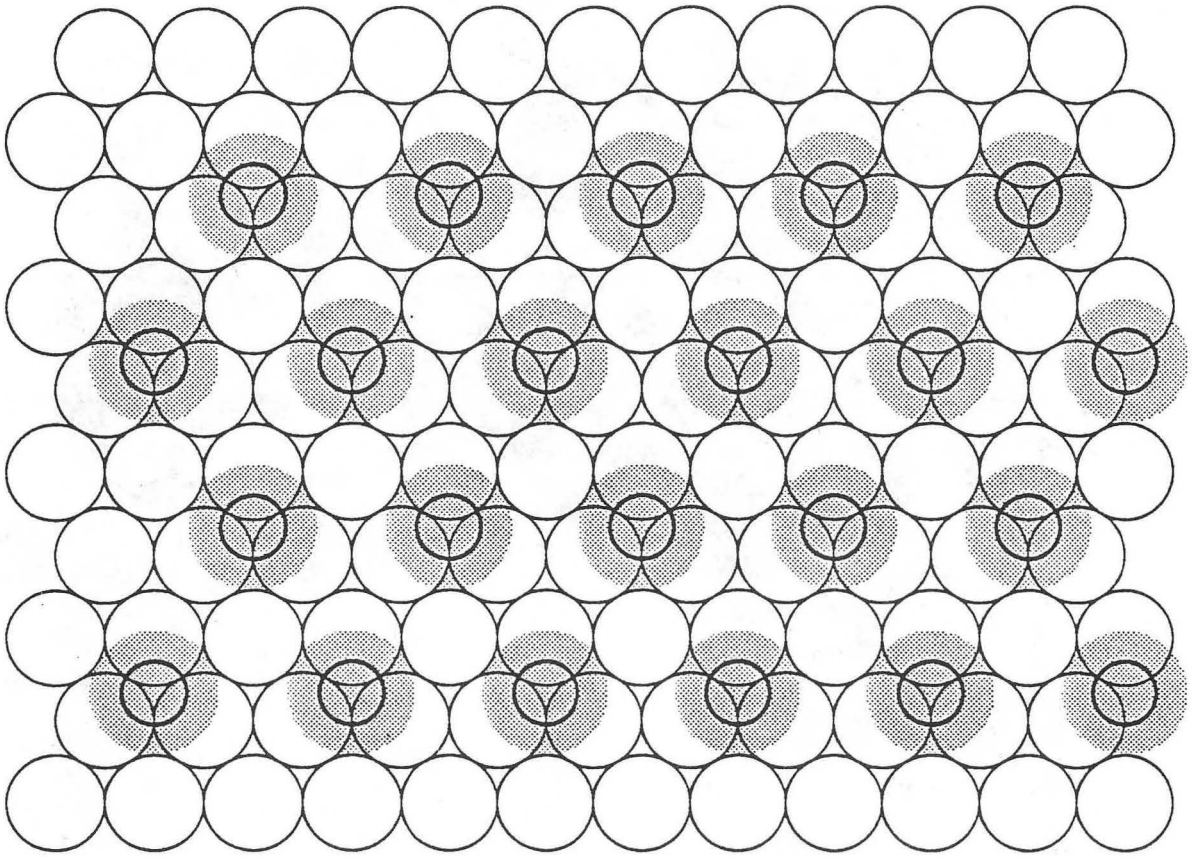
Figure 1(a)



Sulfur 2 x 2 on Re(0001)

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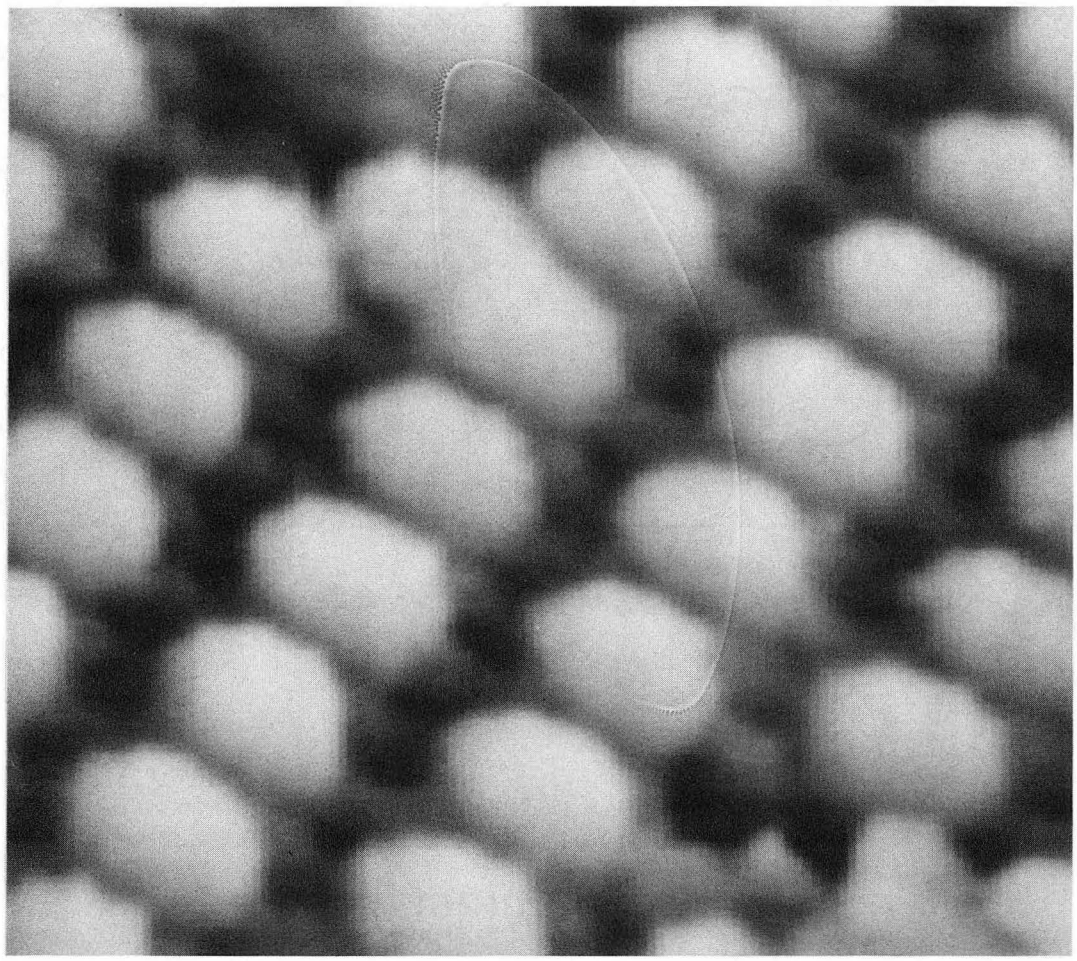
Figure 1(b)

XBL 907-6444



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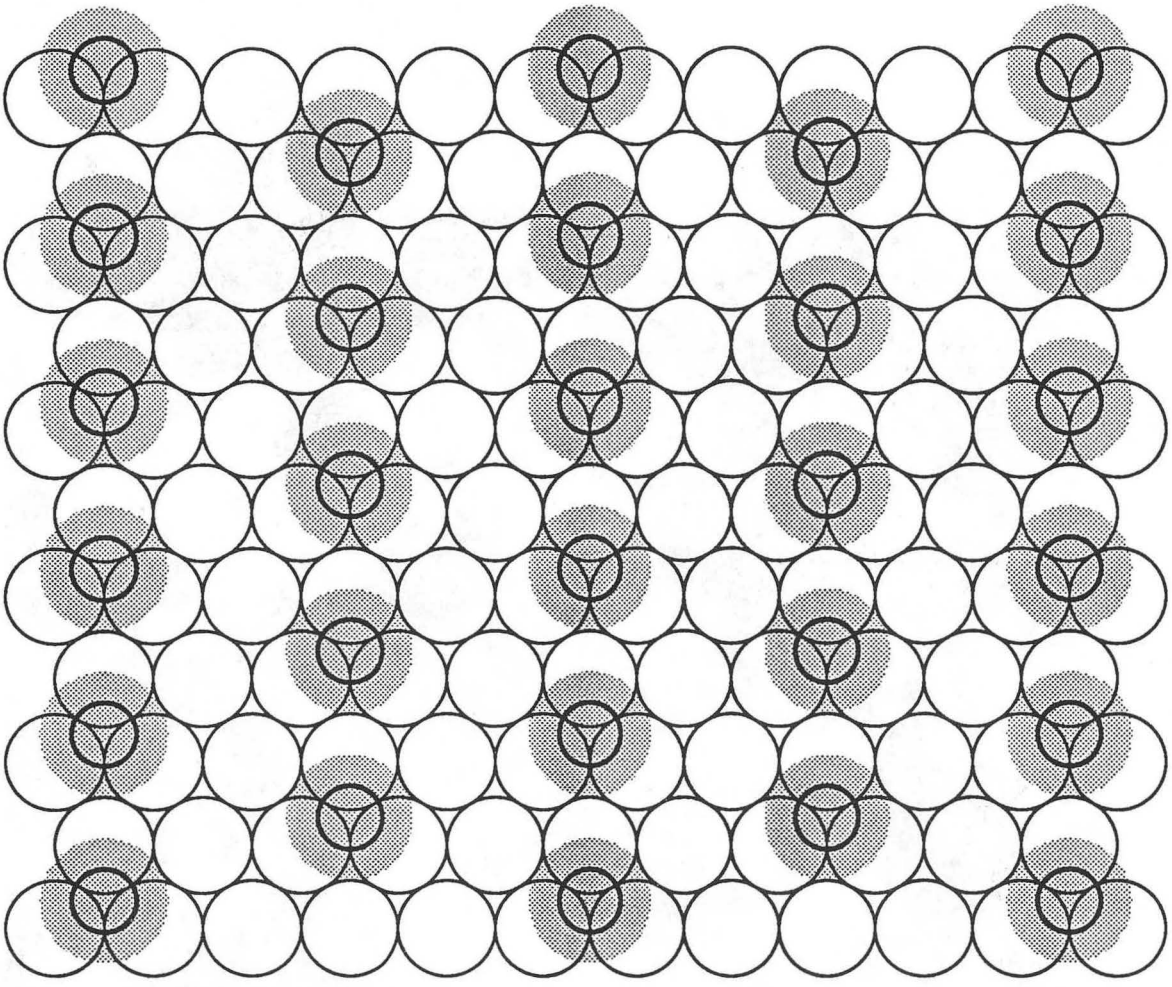

Sulfur c(√3 x 5)rect on Re(0001)

XBL 907-6443

Figure 2b

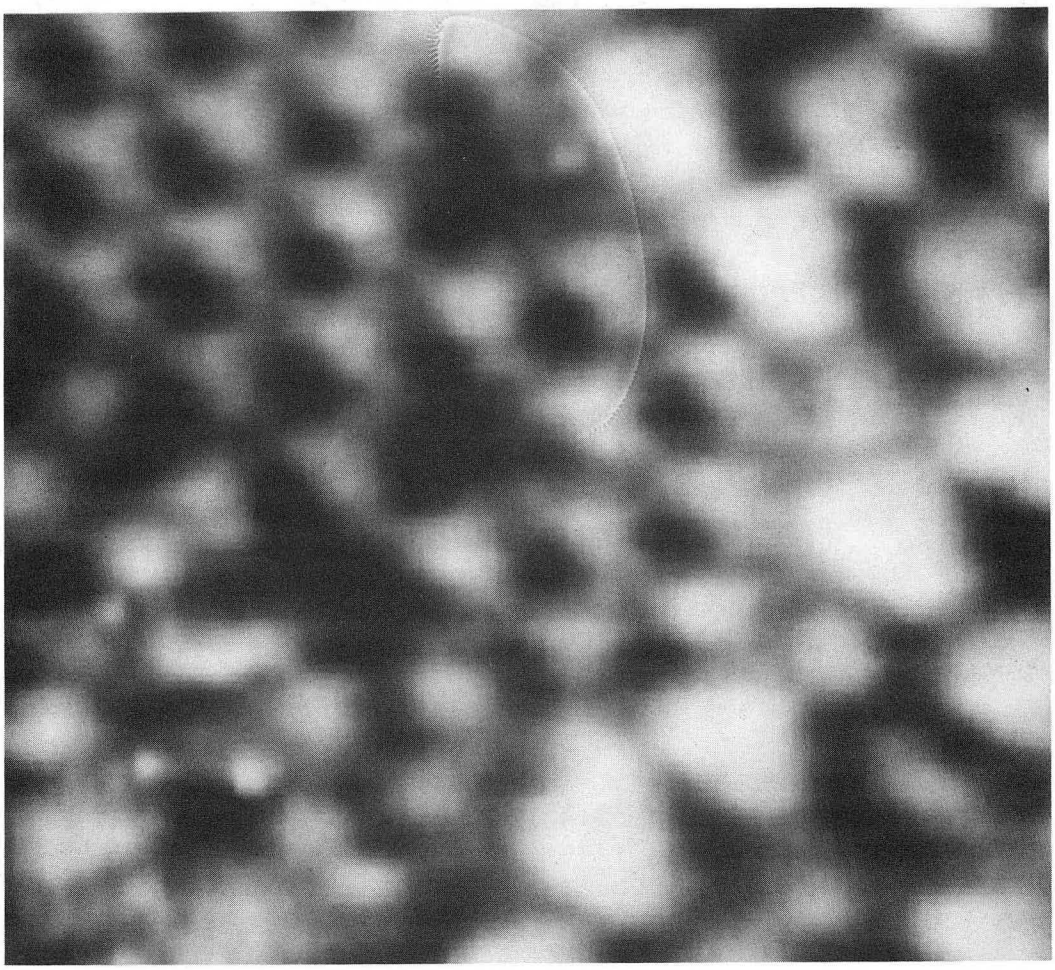

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Figure 3

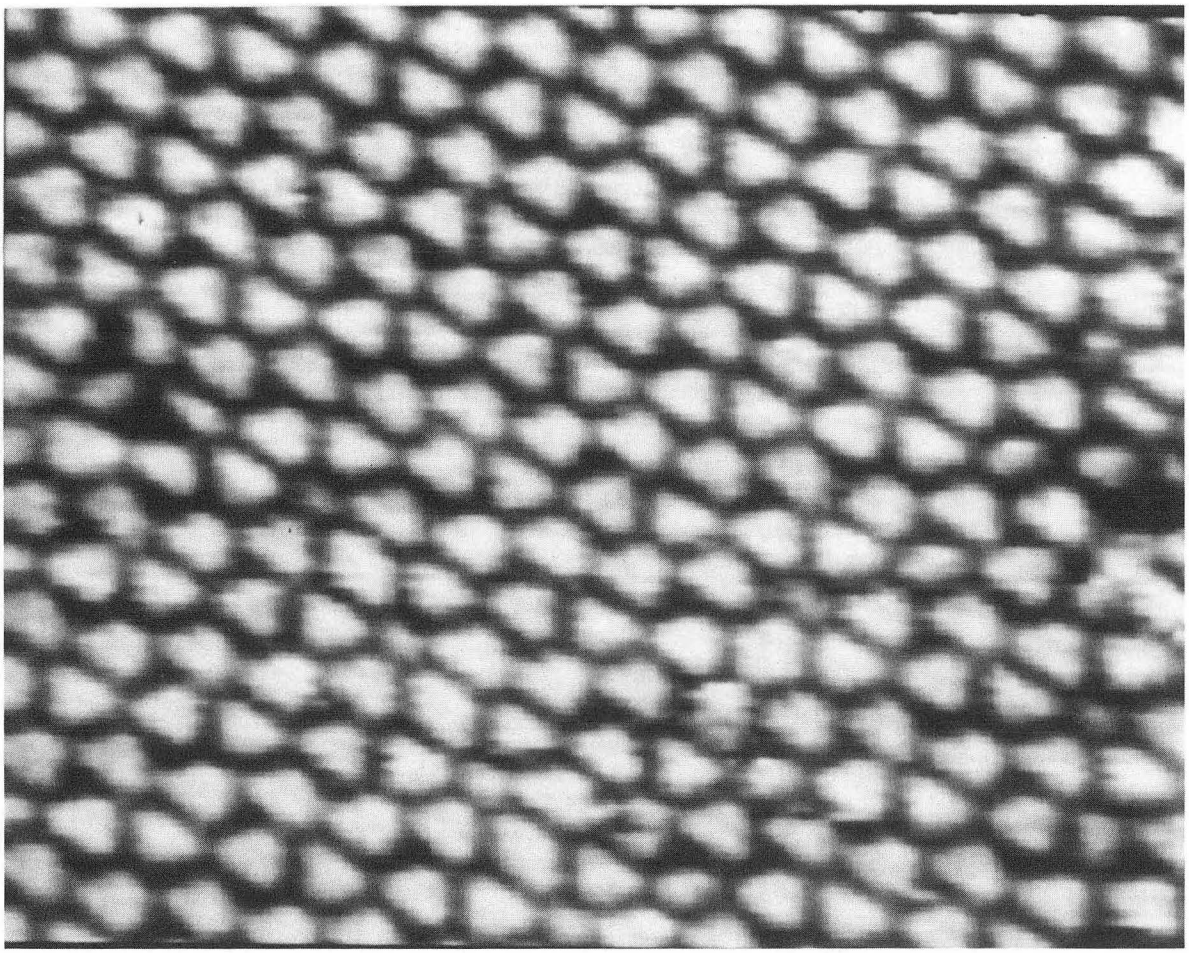

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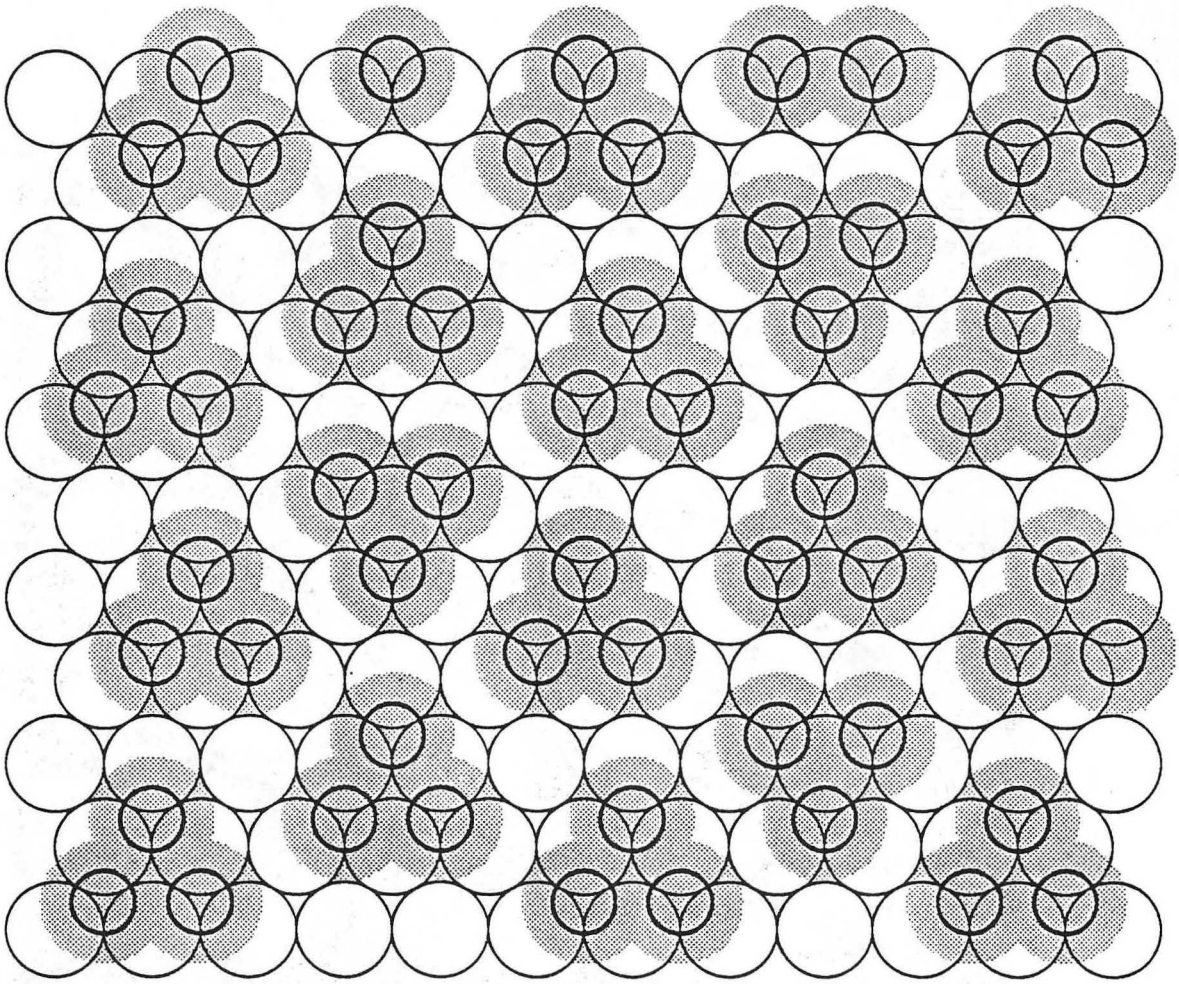
Figure 4(a)



Sulfur $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ on Re(0001)

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Figure 4(b)

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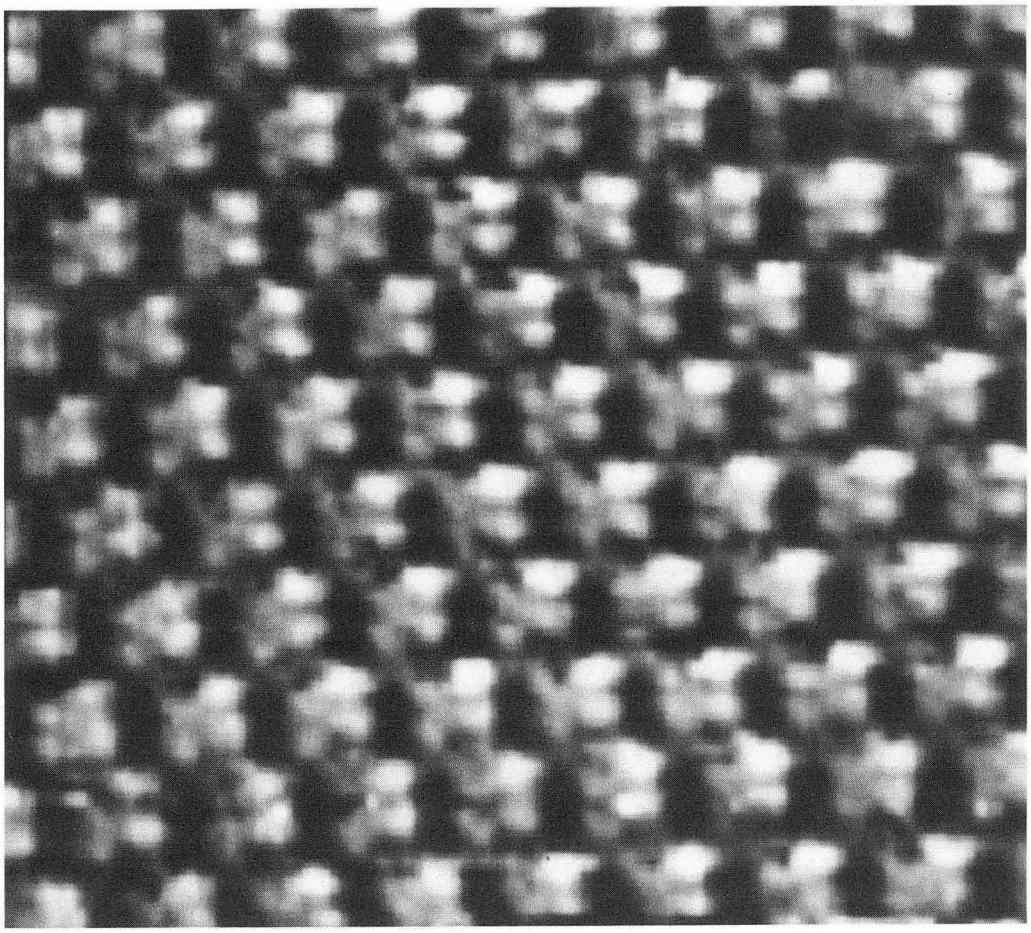

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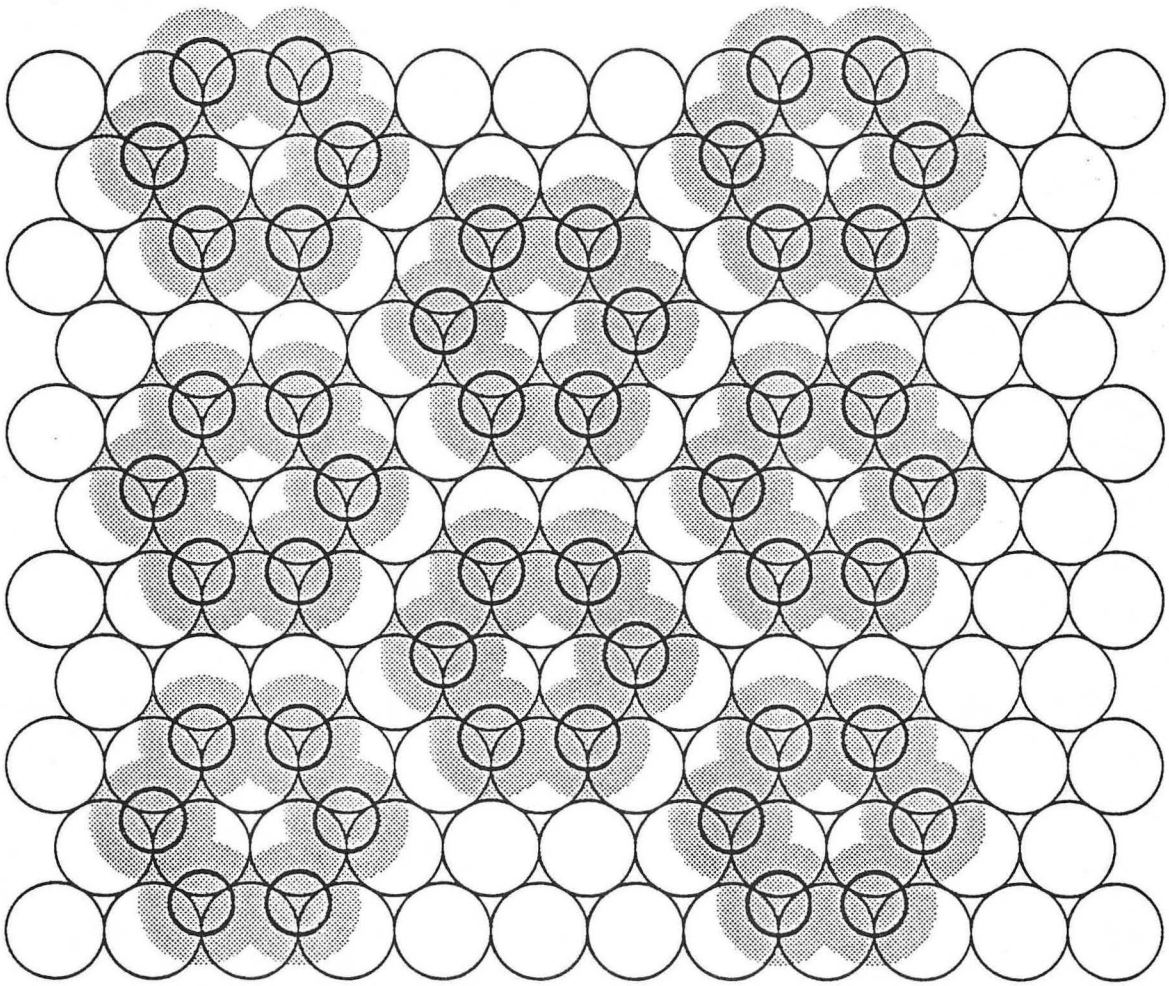
Figure 5(a)



Sulfur $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ on Re(0001)

XBL 907-6447

Figure 5(b)

XBL 907-6447

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