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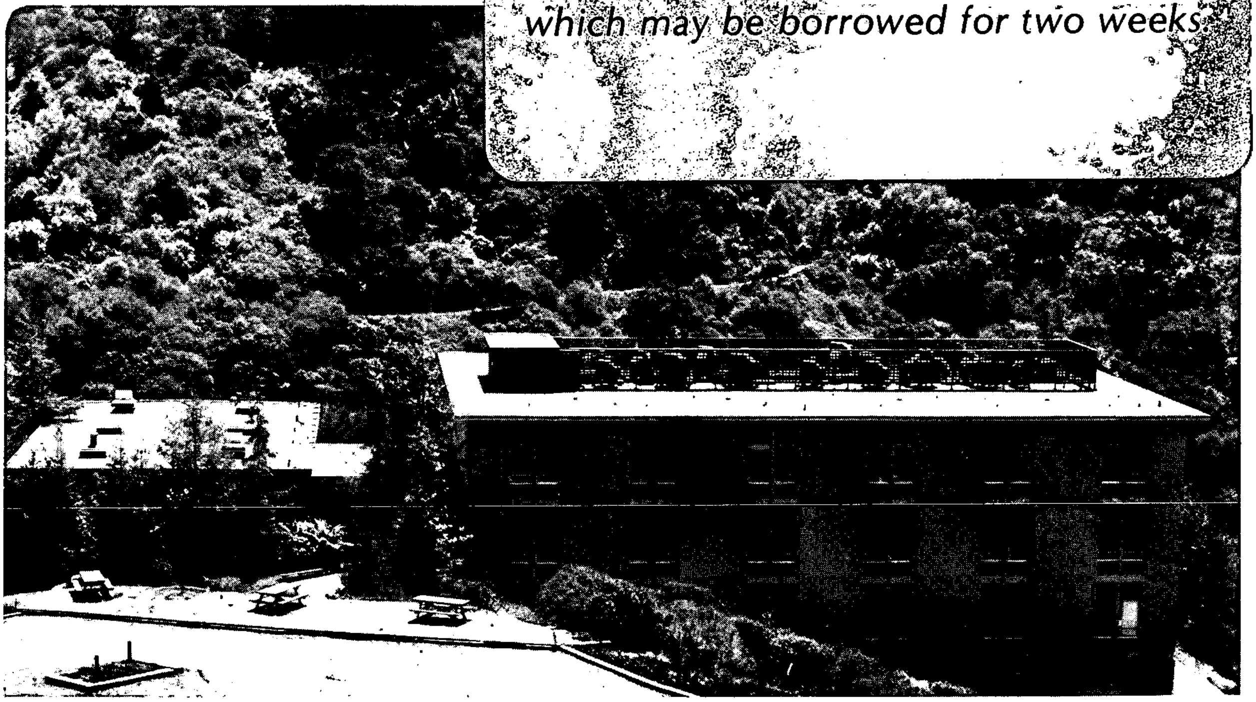

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THE ADSORBATE INDUCED FACETTING OF THE Mo(111) SURFACE

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We have observed the facetting of the Mo(111) surface in the presence of adsorbed nitrogen, oxygen, sulfur and carbon monoxide. The similarities in the surface structural rearrangements observed on going from one adsorbate to another are striking. All facet planes produced have the form (112) x n(111) where n = 0 for oxygen, n = 2 for nitrogen and carbon monoxide and n = 4 for sulfur. The resulting planes are the (112), (334) and (556) surfaces respectively. In the cases of the atomic adsorbates, the component of the (112) plane present in the facet is seen to increase with increasing electronegativity.

There have been a number of reports of facetting of single crystal surfaces of group VIB metals on exposure to various gases, particularly oxygen.[1-7] The interest in these systems stems from the fact that the nucleation and growth of compounds of group VIB metals may be associated with these facetted surfaces. However, little is known about the mechanism of facet formation. Tracy and Blakely attribute their observation of (110) facets on oxidized W(100), W(112) and W(111) surfaces to a reduction in the total surface free energy.[2] Lee and Singer, however, propose that these facets are caused by preferential desorption of the oxide along specific crystallographic directions.[8] It appears that the regularity of the facet formation process on the Mo(111) surface makes it ideal for the study of such phenomena.

In this letter we briefly describe the results of other workers studying the adsorption of N_2, NH_3[9] and CO[10] on the Mo(111) surface and then the results of our studies using O_2[11] and S_2.[12] We will then discuss the nature of the facetted surfaces produced and the regularities that have been observed in the restructuring effects of the different adsorbates. Our work was carried out in two separate UHV chambers each having base pressures in the low 10^{-10} torr range. Each was equipped with Low Energy Electron Diffraction optics, Auger Electron Spectroscopy capabilities and a UTI 100-C mass spectrometer for analysis of background gases. Oxygen exposures were performed by admitting gas into the chamber through a leak valve. Sulfur was deposited in the form of S_2 from an electrolytic source.[13]

The adsorption of nitrogen on the Mo(111) surface has been studied by C. Egawa et al.[9] The adsorption of either N_2 or NH_3 followed by heating to > 850K produced facets composed of (112) x 2(111) planes present in three azimuthal orientations, each rotated 120° with respect to the other two. Nitrogen atoms were adsorbed on these facets at a coverage of $\theta_N = 0.33$ and were present in a c(3x2) superstructure.

The facetting of the Mo(111) surface by CO was first reported by G.C. Berther et al.[10] Adsorption of CO at room temperature followed by annealing to 700K produced (112) x 2(111) facets as in the case of nitrogen. In this case, however, the CO induces a (3x1) superstructure.

Heating the Mo(111) surface to 1050K during an exposure to 3L of oxygen produces facets of (112) orientation. The LEED pattern of this surface appears in Figure 1(a). Each facet has a (1x2) oxygen superlattice with a spacing of one lattice unit in the $[11\bar{1}]$ direction and double spacing in the $[1\bar{1}0]$ direction. A higher exposure of 8L causes the overlayer lattice to be replaced by a (3x1) structure, whose LEED pattern is shown in Figure 1(b).

Annealing to 1000K of a Mo(111) surface that has been sulfided at room temperature yields a surface which produces the complicated LEED pattern shown in Figure 2. This pattern corresponds to a surface having facets formed of (112) x 4(111) planes, again present in three azimuthal orientations. The sulfur present on these planes induces a (3x1) superstructure.

The results described above are summarized in Table 1, along with the electronegativities of the adsorbates. The most striking correlation is that the component of (112) plane present in the facetted surface is apparently dependent on the electronegativity of the adsorbate. The removal of electron density from the surface appears to stabilize the (112) plane and thus the electronegativity of the adsorbate determines the contribution of the (112) plane to the surface area of the facet planes. It is also interesting to note that for all the adsorbates investigated to date the component of the (111) plane present in the (112) x n(111) facets is always characterized by an even value of n (n = 0, 2, 4). Figure 3 shows a view of the (1$\bar{1}$0) surface which is normal to all of the facet planes produced, and its projection onto surfaces with Miller indices of the form (111) and (112) x n(111) for n = 0, 1, 2, 3 and 4.

In all cases the formation of facets required the heating of the Mo(111) surface after room temperature adsorption. Clearly, although the presence of the adsorbate stabilizes these facet planes with respect to the Mo(111) surface, the process is highly activated. The temperature must be high enough to allow facile diffusion of surface atoms.

In all cases the formation of facets occurs at adsorbate coverages that are close to saturation. In the case of oxygen the onset of facet formation precedes the formation of the bulk oxide[11] and thus is probably an important step in this process. The annealing temperatures necessary to produce facets are not so high as to cause significant desorption of material from the surface. In the cases studied here it would seem that preferential desorption of a compound of Mo along a specific crystallographic direction is not the mechanism of facet formation.

The clear regularities observed in the adsorbate induced facetting of the Mo(111) surface make it an obvious system for further study of this process. Continuing work includes the study of other adsorbates such as P, Si, F and Cl. We hope that an examination of the adsorption of these atoms will yield more information about the facetting process.

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FIGURE CAPTIONS

Figure 1 LEED pattern of the (211) facetted surface produced by the adsorption of O_2 on the Mo(111) surface. (a) Oxygen adsorbed in a (1x2) superlattice after 3L exposure to O_2. (b) Oxygen adsorbed in (1x3) superlattice after 8L exposure to O_2.

Figure 2 LEED pattern of the (556) facetted surface produced during the adsorption of S on the Mo(111) surface. (a) 60 eV (b) 50 eV.

Figure 3 The (111) and (112) x n(111) (for n = 0, 1, 2, 3 and 4) surfaces of a b.c.c. crystal projected onto the $(1\bar{1}0)$ plane. Atoms marked with ● lie in the plane of the page while the + marks positions with atoms above and below the plane of the page.

TABLE 1

Adsorbate	Index of Induced Facet Plane		Superlattice	Angle	Electronegativity (Pauling)	Temperature of Facet Formation
O	(112)	(112)+0(111)	(1x2) (1x3)	19.48°	3.5	1050K
N (from N_2 or NH_2)	(334)	(112)+2(111)	c(3x2)	8.05°	3.0	850K
CO	(334)	(112)+2(111)	(1x3)	8.05°	-	700K
S	(556)	(112)+4(111)	(1x3)	5.05°	2.5	1000K

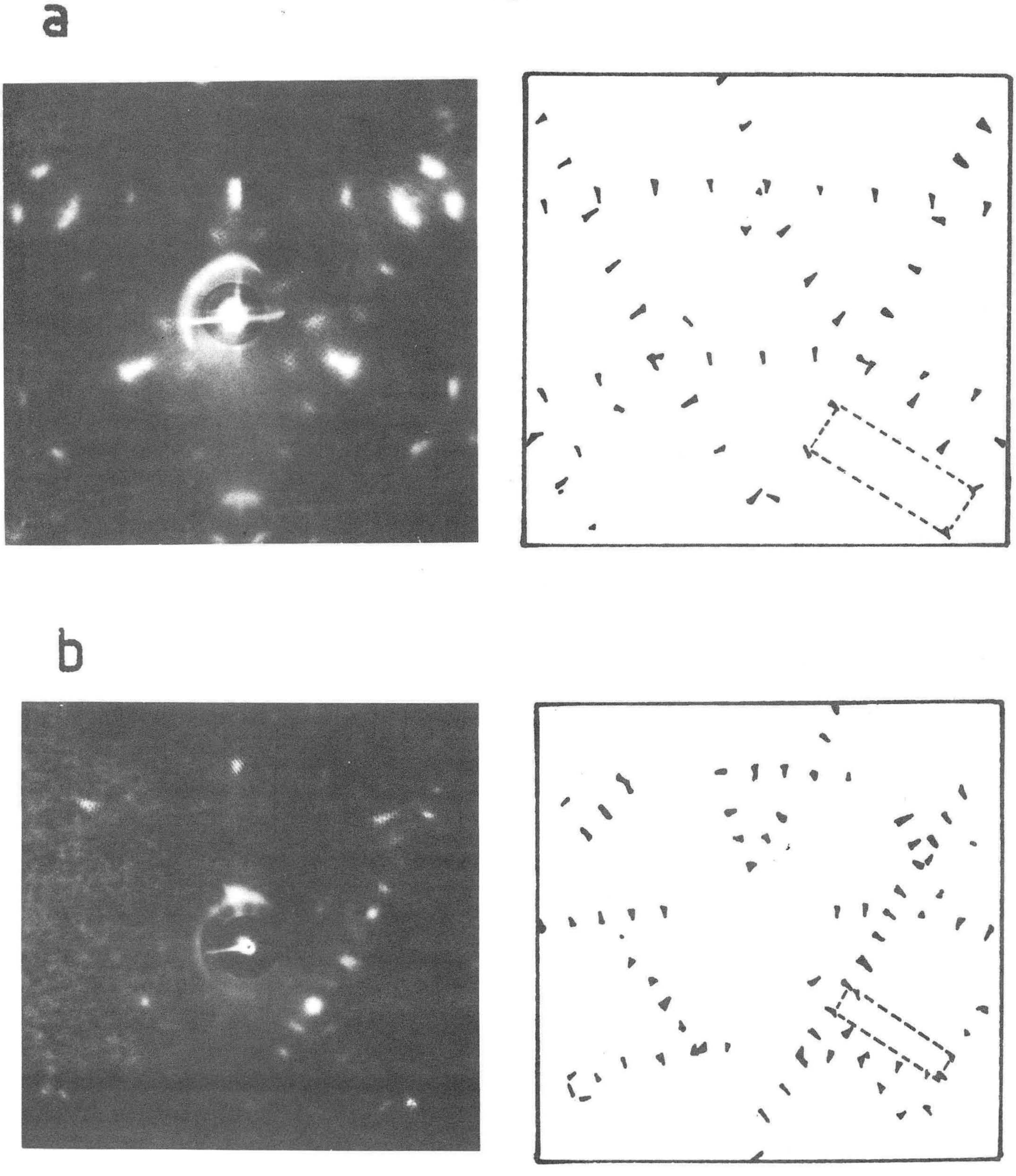

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Figure 1

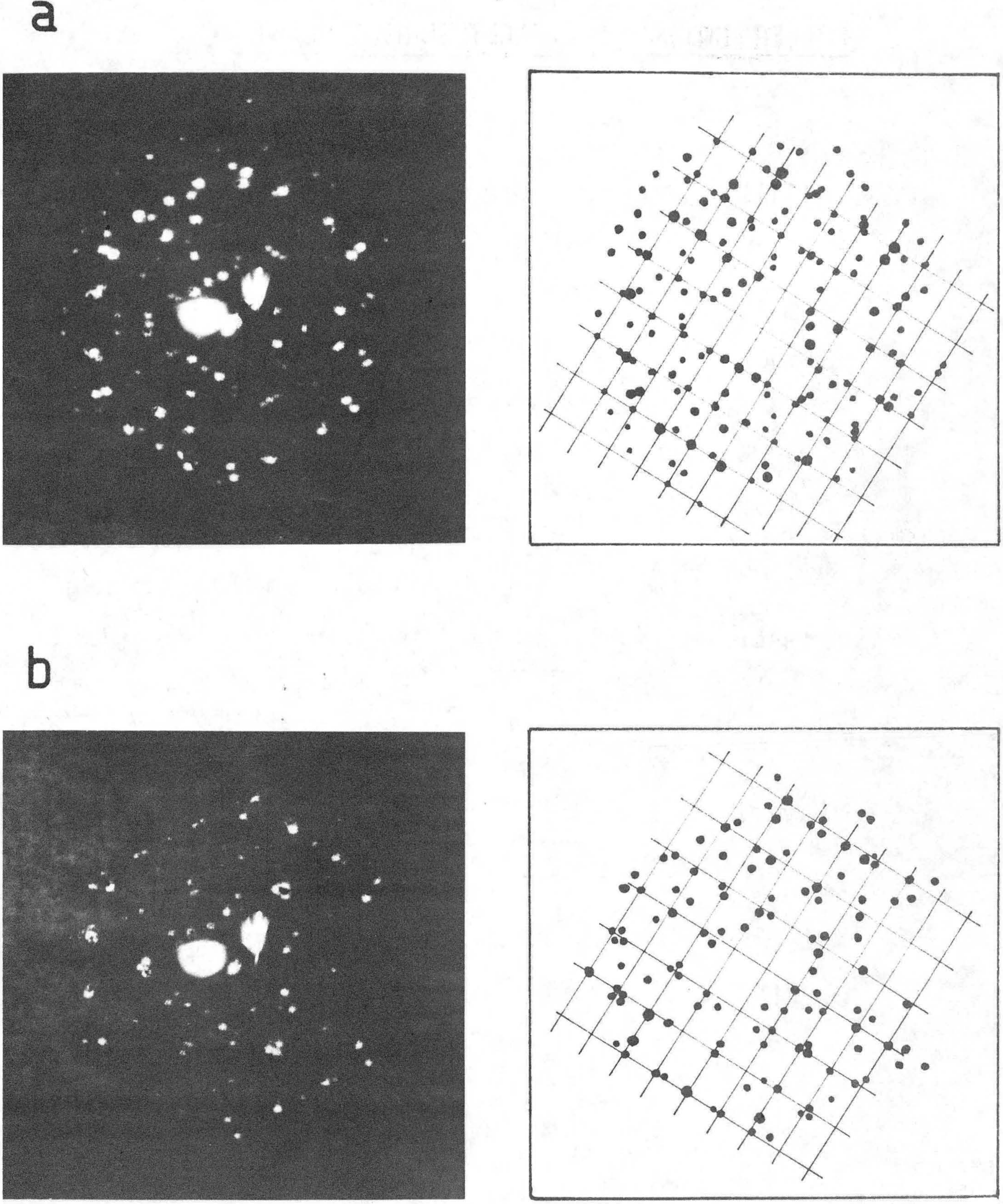

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Figure 2

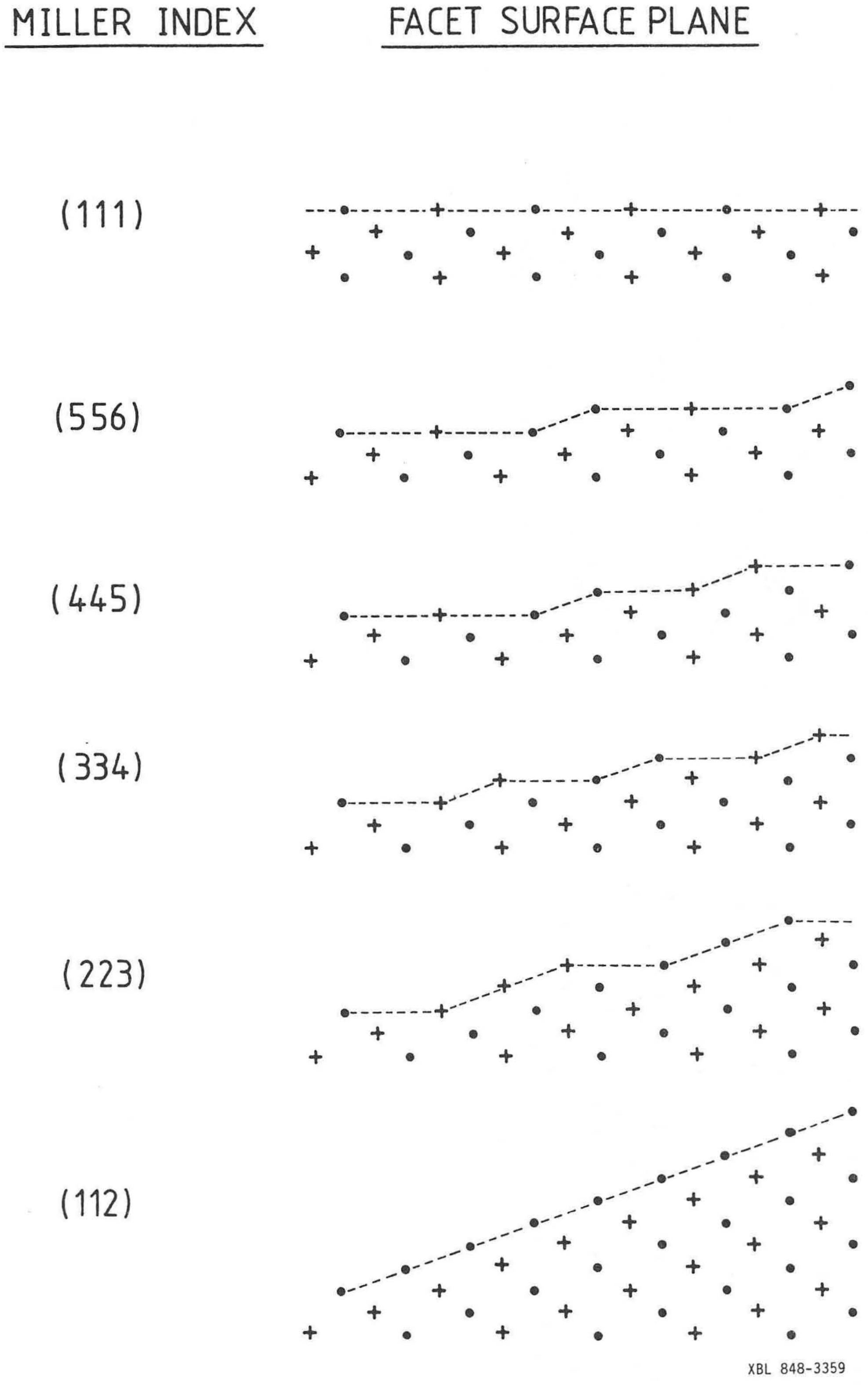
MILLER INDEX
FACET SURFACE PLANE
(111)
(556)
(445)
(334)
(223)
(112)
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Figure 3