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Low Energy Electron Diffraction Studies of High Index Crystal Surfaces of Platinum

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ABSTRACT

Several high Miller Index crystal surfaces of platinum have been examined by low energy electron diffraction (LEED) and have been shown to consist of low index (111) or (100) terraces of constant width, linked by steps of monatomic height. The ordered stepped surfaces were found to be stable in ultra-high vacuum up to 1500°K, and the reasons for this remarkable stability are discussed. The presence of ordered atomic steps may be considered as a general structural property of high index surfaces regardless of the chemical bonding in the crystal. A nomenclature is suggested to identify the surface structures of stepped surfaces.

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INTRODUCTION

Low energy electron diffraction (LEED) studies have been carried out, in general, on close packed crystal faces of low Miller Index. These surfaces are chosen for structural investigation since they have the lowest surface free energy and are therefore stable with respect to rearrangement to other crystal faces or to disordering up to or near the melting point. Studies of surfaces of high Miller Index and higher surface free energy are important in their own right to elucidate their atomic structure and stability under a variety of experimental conditions in the presence of reactive and inert gases and in vacuum.

Recent studies[1-3] indicate that the surfaces of crystals cut to expose a high index plane consist of terraces of low index planes linked by steps often of monatomic height. LEED investigations of copper, germanium, gallium arsenide and uranium dioxide showed ordered step arrays, with terraces of constant width and steps of constant height. The ordered stepped surfaces displayed varying degrees of thermal stability.

The thermal stability and the chemical properties of stepped surfaces are of interest in many areas of surface science. Structural changes which occur may give information about surface phase transformation and surface free energy. If the stepped surface structure is stable in the temperature range where catalytic reactions are carried out (300°-1000°K), the steps may play an important part in surface reaction mechanisms. The structure of chemisorbed layers is also likely to be different on stepped surfaces.

In this paper we report on LEED investigations of the surface structure of three high index surfaces of platinum. Crystals cut at small angles from low index planes developed ordered step structures, the terrace/step geometry reflecting the cutting angle. Since the steps are ordered the LEED technique is very suitable for their study. Platinum step structures were found to have remarkable thermal stability; thus they may play an important role in surface catalyzed reactions, at least at temperatures below 1500°K. The possible reasons for the thermal stability of these surfaces are discussed and their usefulness in studies of the orientation dependence of surface free energy (γ) is indicated.

EXPERIMENTAL

Platinum single crystals[4] containing 50 ppm of metallic impurities and 100 ppm of non-metallic impurities were used. Samples were cut by sparkmachining at 6.5° from the (111) face towards the (111) plane; 9.5° from the (111) face towards the (100) plane; and 9.0° from the (100) face towards the (111) plane. They were mechanically polished with (1/4)μ alumina and etched in 50% aqua regia. The orientations were determined by the back reflection Laue X-ray technique with an accuracy of ± 1/2° and were checked at each stage of the crystal preparation. Figure 1 shows the directions of the cuts in the crystallographic zones, together with the X-ray Laue pattern of one of the crystals. The crystals were mounted on platinum supports.

Two Varian ultra-high vacuum systems were used in these studies, each being routinely capable of pressures $<10^{-9}$ torr; LEED patterns were

monitored using Varian 4-Grid optics. Auger Electron Spectroscopy (A.E.S.) measurements, using a Vacuum Generators analyser attached to the LEED optics, indicated that graphitic carbon and carbon monoxide were the most common contaminants and were not always removed from the surface by ion bombardment. Clean platinum surfaces, as indicated by A.E.S., were generated by heating in oxygen (1×10^{-7} torr) at 850°C for an appropriate time (10-60 minutes). Production of an atomically clean platinum surface is discussed elsewhere.[5] Auger spectra of clean platinum agree well with those reported by Palmberg.[6]

On removal of the crystals from the vacuum chamber the X-ray patterns were found to be unchanged.

RESULTS

Figure 2 shows the diffraction patterns from the clean stepped surfaces. The stepped surfaces with (111) terraces have the usual (1x1) surface structure. The stepped surface with (100) terraces has the (5x1) surface structure commonly found on the Pt(100) crystal face,[7a] but there is only one domain with its period of five normal to the step direction. The patterns differ from those expected from crystals with low index faces only in that the spots are split into doublets at certain voltages. It has been shown[1-3] that this splitting is a function of ordered steps existing on the surface. The diffraction features are as sharp as those observed with a nominally flat, low index surface. In the case of (100) terraces with a (5x1) surface structure, the doublet spots are not easily detectable because of the high spot density.

However on adsorption of CO or H_2, which eliminates the (5x1) diffraction features, the doublet spots characteristic of the ordered steps are readily discernible.

The intra-doublet separation is dependent on the distance between steps (i.e., the terrace width) and kinematic analysis shows that the intensity distribution within the doublets is a function of step height.[3] Thus, for the 00 spot, the voltages at which a singlet spot exists with maximum intensity are given by the equation:

$$V_{00}(\text{Singlet Max.}) = \frac{150}{4d^2}(S^2) \qquad (1)$$

where d is the step height and S is an integer. For half-integral values of S doublet spots of equal intensity exist. Since V_{00}(Singlet Max.) is inversely proportional to d^2, the voltage dependence is a sensitive measure of step height, which can easily be determined.

The terrace width as calculated from the doublet separation of the 00 beam is given in Tables I and II for two crystal faces used in this study, together with that predicted from the cutting angle; good agreement exists, so that the surfaces can be identified by the angle of the original cut. Tables I and II also give the voltages for singlets of maximum intensity [V_{00}(Singlet Max.)] and doublets of equal intensity [V_{00}(Equal Doublet)] for the respective crystals, together with those predicted assuming monatomic step height. Again good agreement exists, although no account has been taken of the inner potential.

Thus the high index surfaces consist of terraces of low Miller Index linked by steps of monatomic height. Schematic diagrams of the stepped

surfaces corresponding to the diffraction patterns of Fig. 2 are shown in Fig. 3. Indices give little physical insight into the atomic structure of stepped surfaces, so a suitable convention for the nomenclature of these surfaces has been devised and is detailed in an appendix to this paper. Using this approach the surfaces examined here are designated in Table III. Each of the ordered step structures is stable in vacuum up to 1500°K and is readily reordered by heating after ion bombardment. Heating the Pt(S)-[9(111) x (111)] crystal to 950-1100°K in 10^{-5} torr of oxygen followed by cooling in oxygen caused elongation of the doublets, as is shown in Fig. 4. This indicates disordering of the surface, with terrace widths now greater and less than 9. Removal of the adsorbed oxygen by heating in vacuum at 800°K restored the surface to its original ordered state. It should be noted that chemisorption of oxygen on the low index planes of platinum has not been observed, while it readily occurred at the stepped surfaces of platinum. Hydrogen showed preferential adsorption at the atomic steps at low temperatures (300-900°K). Hydrogen adsorption takes place only at the highest temperatures ($>$1300°K) and pressures ($> 10^{-5}$ torr) on the Pt(100) face[7a] and reports indicate that similar high temperatures and hydrogen pressures are necessary for the ordered chemisorption of hydrogen on the Pt(111) face.[7b] Detailed results of chemisorption and reaction at the steps will be reported in a subsequent paper.[8]

DISCUSSION

Platinum crystals cut in different crystallographic zones at small angles from (111) and (100) planes possess surfaces of ordered steps of monatomic height which show remarkable thermal stability. These ordered steps have been noted on other metals and on semi-conductors and thus must be a general property of high index surfaces of all types of crystalline materials.[1-3]

It is of interest to examine the thermodynamic stability of this type of surface with respect to that of the lowest free energy, low index surface. The variation of surface free energy with orientation is described by a polar γ-plot in which a vector $\underline{n}$ in a particular crystallographic direction has magnitude proportional to the surface free energy (γ) in that direction. Herring[9] has shown that at 0°K the γ plot has cusps (local minima in γ) for each plane of rational Miller Index and has indicated that as the temperature increases most of the cusps disappear. At higher temperatures, for example 700°K, only those directions corresponding to low index planes will possess cusps. Winterbottom[10] has stated that the high temperature polar plot for platinum has minima only for the (111) and (100) planes. Therefore the terraced surfaces considered here are not thermodynamically stable with respect to the (111) and (100) surfaces of platinum. The stepped surfaces may, on these grounds, be expected to disorder at temperatures where this study has shown them to be stable. The remarkable thermal stability which has been observed is likely to be due to the difficult routes which the crystal must take to develop an equilibrium shape.

There are only two ways in which the ordered surface can transform into a low free energy (111) or (100) face, namely thermal faceting or disordering and rearrangement by surface diffusion.

In the case of thermal faceting the surface would transform into a hill and valley network of intersecting low index faces. The available criteria for this to occur[11] indicate that for a surface at an angle α to a low index surface:

$$-\frac{1}{\gamma}\frac{\partial^2\gamma}{\partial\alpha^2} < 1$$

McLean and Mykura[12] have examined the stability of platinum foils of various orientations towards thermal faceting. They have estimated γ for various α using the technique based on measuring angles at twin boundaries. They conclude that surfaces close to the (111) orientation are stable with respect to faceting up to 1900°K, in agreement with this study. Surfaces close to the (100) face were found to be less stable, faceting above 1500°K. Their platinum surfaces were not cleaned in ultra-high vacuum and in consequence were probably covered with several monolayers of graphitic carbon. Nevertheless, from the relationship between faceting and $\frac{\partial\gamma}{\partial\alpha}$ the orientations herein considered are not expected to undergo thermal faceting.

We now consider the possiblity that the surfaces may seek a thermodynamically stable arrangement by surface diffusion. Burton, Cabrera and Frank[13] considered surface roughening by the formation of kinks and suggested the existence of a critical temperature T_c above which complete

roughening of the surface will occur. Winterbottom has suggested that T_c may be about one half of the melting point, for platinum about 1000°K.[10] McLean and Mykura,[12] however, could detect no evidence of surface roughening of platinum foils, nor was roughening indicated in this study. It seems likely that earlier ideas on the critical temperature for surface roughening should be modified. In the case at least of face centered cubic metals, the results of various studies on platinum and copper[2] suggest that T_c for the (111) face may be close to the melting point of the metal. Low energy electron diffraction studies of ordered stepped surfaces of semi-conductors (diamond structure) by Henzler[3] provide good evidence of the instability of certain stepped surfaces towards surface diffusion.

The effect of surface diffusion has been treated from a different standpoint by Schwoebel and Shipsey,[14] who consider a stepped array similar to that treated here. They examine the time dependent change in terrace width as a function of the capture probability at the step of atoms arriving from different directions. Thus a diffusing atom arriving at the step from the right is assumed to have a different probability of incorporation into the step compared to an atom arriving at the step from the left. Their calculations show that, for an array of constant step height and terrace width, the structure is time independent, i.e., it is stable under conditions of surface diffusion. This result is of obvious importance for the interpretation of our studies of stepped surfaces of platinum, since diffusion of platinum atoms on the surface is known to be rapid at temperatures as low as 900°K, the temperature at which ion bombarded surfaces can be annealed. The calculations of Schwoebel and Shipsey predict that ordered stepped

surfaces will remain stable even in the presence of the considerable surface diffusion which is known to occur.

We may now see why the ordered stepped surfaces do not transform into the lower free energy, more stable, low index faces. Because of the shape of the γ plot the surfaces consideredhere are stable with respect to thermal faceting. In addition the surfaces should be stable under conditions of surface diffusion. As has been suggested above, no energetically feasible route is likely to exist by which the array of ordered steps may rearrange to a thermodynamically more favorable surface structure.

It is of interest to consider the degree of disorder on the atomic scale which would be detectable from LEED observations; this question has been considered in detail by Houston and Park[15] in a recent paper dealing specifically with the effect of stepped surfaces on LEED patterns.[16] These authors indicate that a well-ordered diffraction pattern such as is reported here may arise even from a rather disordered array of steps. Because of this and the disorder known to arise from the mechanical preparation of single crystal surfaces, it is not our contention that the stepped surfaces possess perfect order on an atomic scale. It is suggested, nevertheless, that LEED is a useful indicator of the greatest degree of order at the surface. The technique differentiated easily between two crystals, one cut at an angle of 6.5° and the other at an angle of 9.5° to the (111) plane. It has also been shown that gross disorder, resulting for example from oxygen treatment, is detected in the diffraction pattern. Future examination of this type of surface by LEED, in conjunction with the

analytical techniques suggested by Houston and Park, may yield detailed information on surface topography.

The thermal stability of ordered stepped surfaces indicates that they are likely to be present on metal particles that are commonly used as catalysts in surface chemical reactions. The presence of steps changes the nature of chemisorption and thus plays an all-important role in subsequent surface reactions. Indeed studies in this laboratory have revealed the chemisorption and ordering of several gases that would not chemisorb or order under the same conditions on low index (111) and (110) crystal faces of platinum. Adsorption occurs preferentially at the steps and ordering of the adsorbed atoms is nucleated at the steps. These studies, to be reported in detail in a subsequent paper,[8] are of significance in the field of heterogeneous catalysis. The atomic structure of stepped surfaces should be similar to the atomic surface structure of polydispersed catalytic particles on porous supports. It is believed that LEED studies of surface reactions on ordered stepped surfaces will yield the structural information so far lacking and necessary to elucidate the mechanisms of catalytic surface reactions.

ACKNOWLEDGEMENTS

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TABLE I

Pt(S)-[6(111)x (100)] surface: voltages for singlets of maximum intensity and doublets of equal intensity and terrace width.

S (from Eq.1)	V_{00}(Singlet Max.) calc.	V_{00}(Singlet Max.) meas.	V_{00}(Equal Doublet) calc.	V_{00}(Equal Doublet) meas.	Terrace Width (number of periods) calc.	Terrace Width (number of periods) meas.
2	29	29				
2.5			46	47	$5+\frac{2}{3}=5.67$	5.87
3	66	68				
3.5			90	89		
4	118	123				
4.5			149	163		
5	184	193				
5.5			222	225		
6	265	273				
6.5			311	315		

TABLE II

Pt(S)-[9(111) x (111)] surface: voltages for singlets of maximum intensity and doublets of equal intensity and terrace width.

S (from Eq.1)	V_{00}(Singlet Max.) calc.	V_{00}(Singlet Max.) meas.	V_{00}(Equal Doublet) calc.	V_{00}(Equal Doublet) meas.	Terrace Width (number of periods) calc.	Terrace Width (number of periods) meas.
2	29	33				
2.5			46	51	$8+\frac{1}{3}=8.33$	8.75
3	66	67				
3.5			90	90		
4	118	125				
4.5			149	159		
5	184	190				
5.5			222	237		
6	265	270				
6.5			311	326		

TABLE III

Angles of cut, Miller Index, and designation of three stepped surfaces of platinum.

Angle of cut	Miller Index	Designation
6.5° from (111)	(997)	Pt(S)-[9(111) x (111)]
9.5° from (111)	(755)	Pt(S)-[6(111) x (100)]
9° from (100)	(911)	Pt(S)-[5(100) x (111)]

APPENDIX

Nomenclature for Ordered Stepped Surfaces

The appearance of ordered stepped surfaces has been observed on germanium,[3] gallium arsenide,[3] copper,[2] uranium dioxide[1] and on platinum. Since the rearrangement to ordered low index terraces seems to take place regardless of the chemical bonding in the crystal, it may be regarded as a general structural property of high index surfaces. As studies of this type of crystal are likely to become more important, it would be of value to have a standardized nomenclature to identify stepped surface structures and we would like to propose one which we have found convenient.

A stepped surface is indicated by the postscript (S), so the Pt(S) indicates a stepped platinum crystal surface. The ordered step array can then be completely designated by the width and orientation of the terraces and the height and orientation of the steps. We suggest that this information be presented as:

$$Pt(S)\text{-}[m(111) \times n(100)]$$

where m(111) designates a terrace of (111) orientation, m atomic rows in width, and n(100) indicates a step of (100) orientation and n atomic layers high. For example the stepped surface shown in Fig. 3b is designated as Pt(S)-[6(111) x 1(100)]. In the case of steps of monatomic height the prefix n=1 may be omitted. Thus a surface may be designated as Pt(S)-[6(111) x 1(100)] or as Pt(S)-[6(111) x (100)].

A problem arises when the step may be assigned two orientations. Thus, if the step in Fig. 3a is defined by the rows AA' and BB', its

orientation is (110). If, however, the step is defined by the rows AA' and CC', its orientation is (111). This problem can be solved if we define the step by the plane which makes the smallest angle with the terrace normal. In this way the step is AA'-CC' with a (111) orientation. Consideration of various ball models of stepped surfaces suggests that this is the most realist view of the terrace/step geometry.

It is also valuable to characterize the surface structure of the adsorbed molecules on the stepped surface, particularly in the case where the structure of the adsorbed layer is nucleated at the step or the steps participate in the formation of the surface structure. If the adsorption structure is not restricted to the step and its unit cell is related only to the unit cell of the terrace plane, the standard notation can be used. Thus Pt(S)-[9(111) x (111)]-(2x2)-H indicates a stepped surface with hydrogen adsorbed on the terrace planes in a (2x2) unit cell.[8]

The simplest case of adsorption which is nucleated at the step is the case in which ordered adsorption occurs only at the step. We suggest the use of, for example Pt(S)-[6(111) x (100)]-2(1d)-H to indicate a one-dimensional hydrogen structure at the steps of a platinum surface, the one-dimensional repeat distance being twice the period of the platinum atoms in the step.[8] The notation 1d is often used to designate one-dimensional ordered surface structures.

The remaining and most complex case is when the adsorbed layer has a unit cell which is a multiple of the unit cell of the stepped surface. Perdereau and Rhead[2] have reported examples of surface structures with

rather large unit cells overlapping one or more terraces. The notation suggested by these authors may lead to difficulties and we suggest the following modification. Fig. 5 shows several examples of unit cells of various surface structures on a stepped surface. The letter s is used to indicate that a structure is referred to the unit cell (s x 1) of the clean stepped surface and not to the unit cell (1 x 1) of the terrace plane, as in the previous cases (Fig. 5). The unit cell (s x 3) covers one terrace and is expanded three times parallel to the step direction. The unit cell (2s x 1) overlaps two terraces, while keeping the periodicity of the clean stepped surface parallel to the step direction.

FIGURE CAPTIONS

Fig. 1a. Crystallographic orientations of the high index faces of platinum which were examined in this study.

1b. X-ray Laue pattern of the (911) crystal face of platinum.

Fig. 2. Diffraction patterns of the various clean stepped surfaces of platinum:

a. Pt(S)-[9(111) x (111)], 140 V

b. Pt(S)-[6(111) x (100)], 140 V

c. Pt(S)-[5(100) x (111)], 68 V

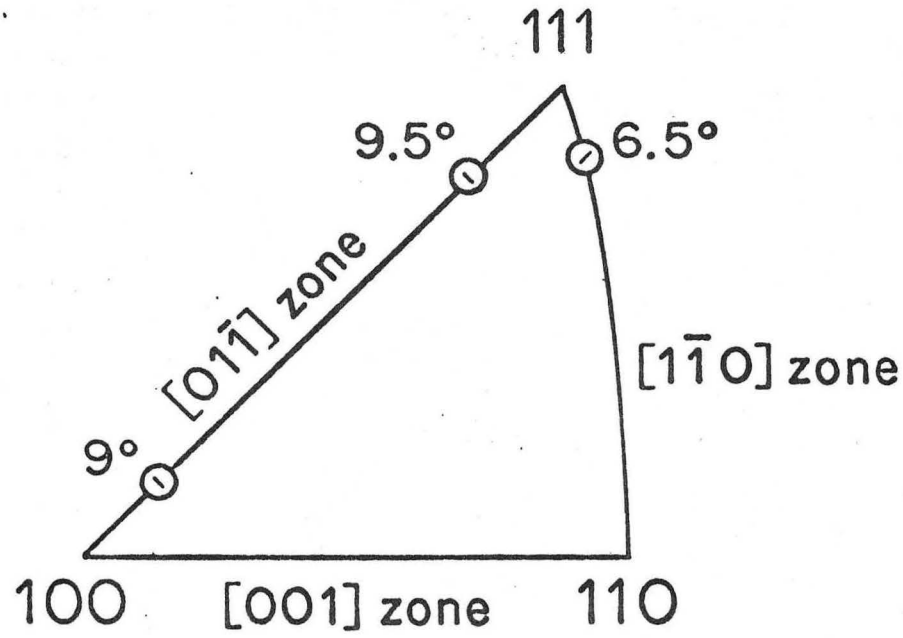
Fig. 3. Schematic representation of the atomic structures of two stepped surfaces:

a. Pt(S)-[9(111) x (111)]

b. Pt(S)-[6(111) x (100)]

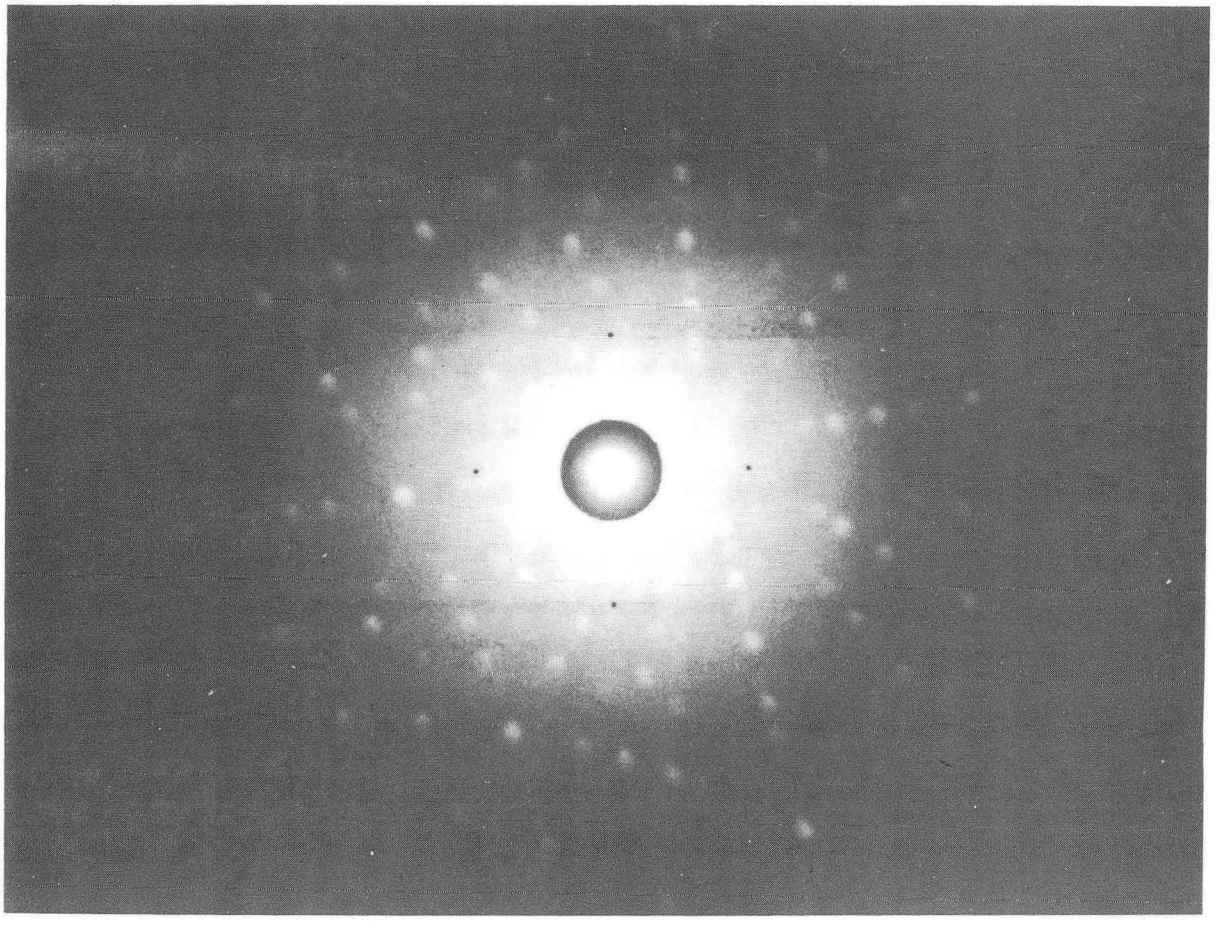
Fig. 4. Diffraction pattern of the Pt(S)-[9(111)x(111)] surface after heat treatment in oxygen, 95 V.

Fig. 5. Examples of unit cells of various surface structures on a stepped surface.



XBL 718-1270

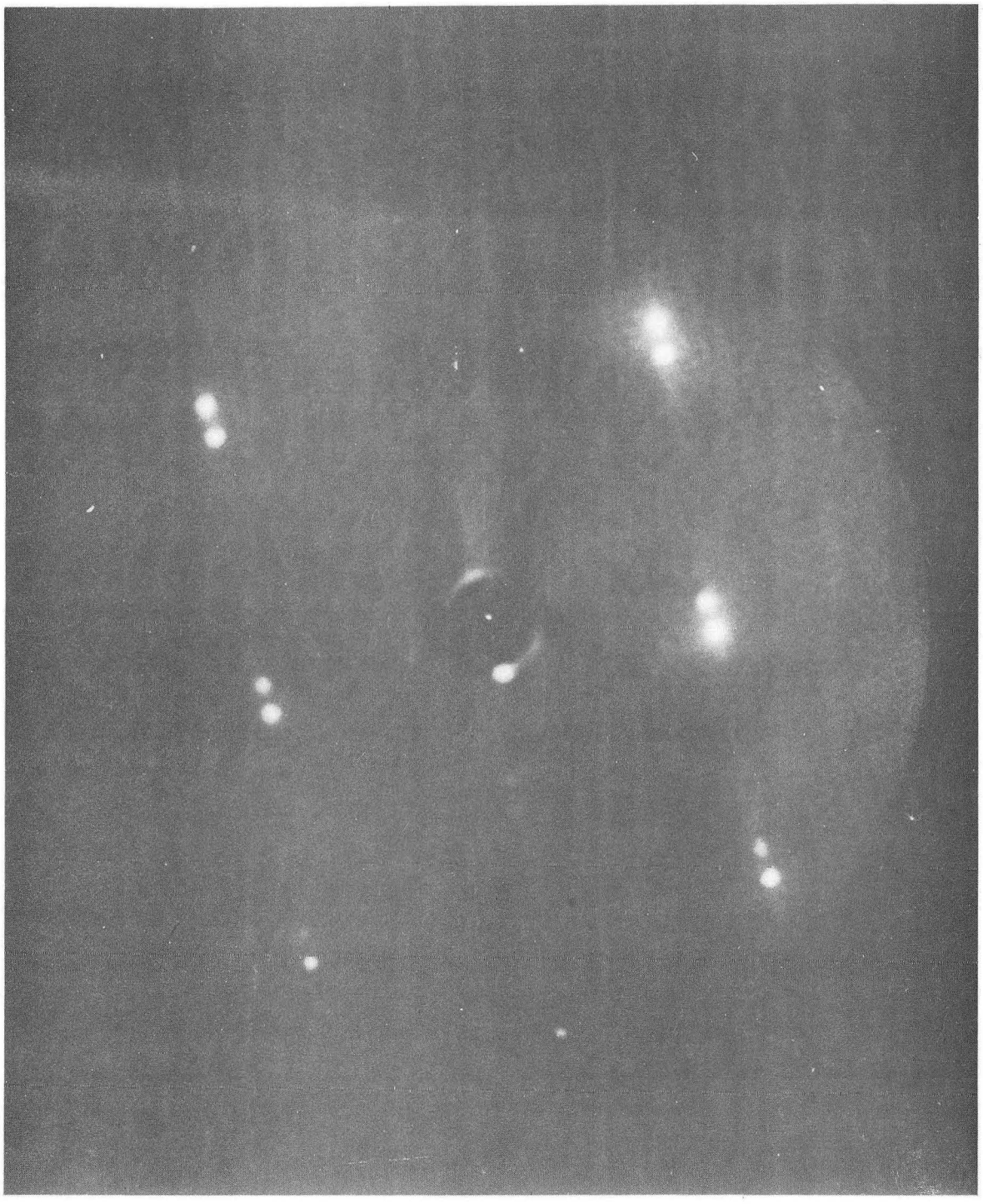
Fig. 1a



XBB 719-4456

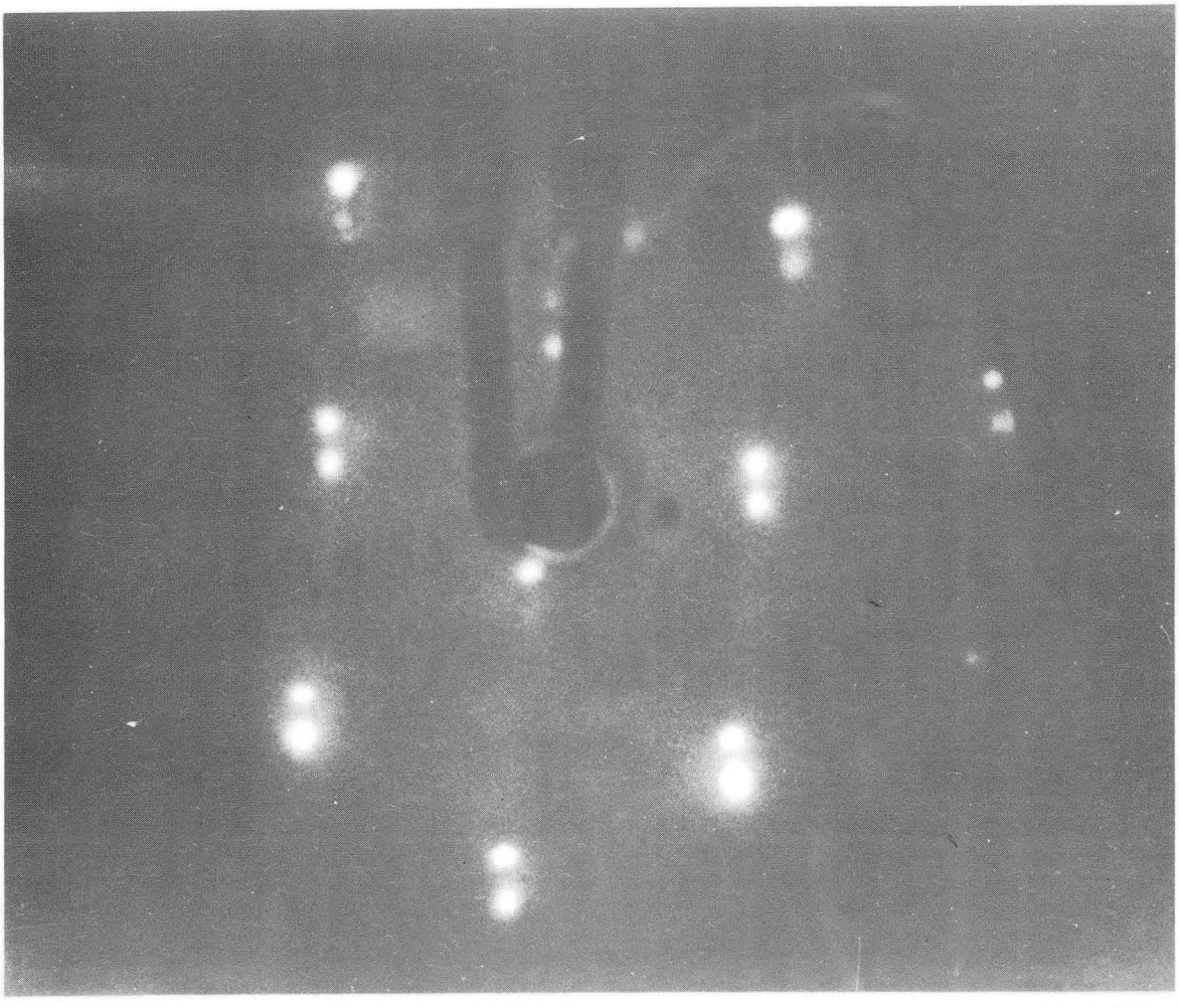
Fig. 1b

0 0 0 0 3 6 0 3 3 3 7



XBB 719-4596

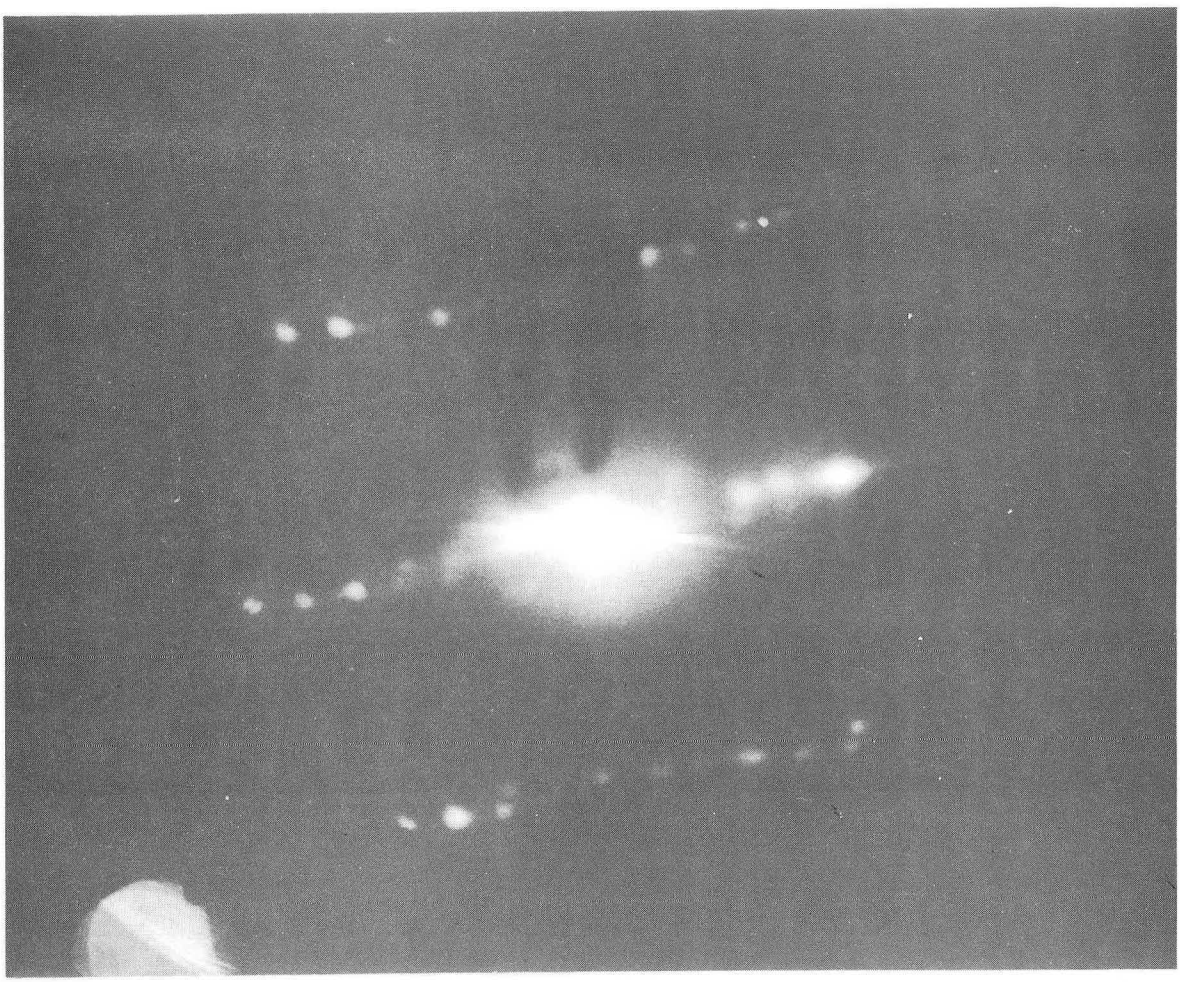
Fig. 2a



XBB 7110-4951

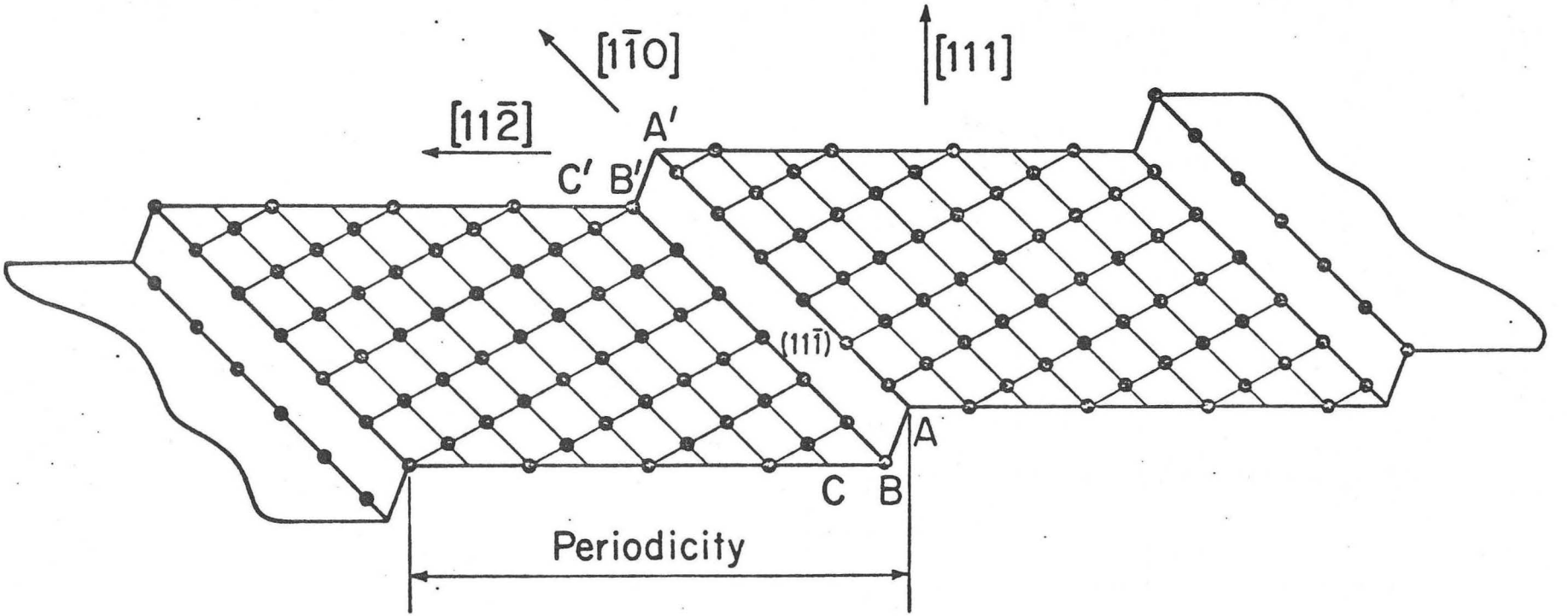
Fig. 2b

0 0 0 0 3 6 0 3 3 3 8



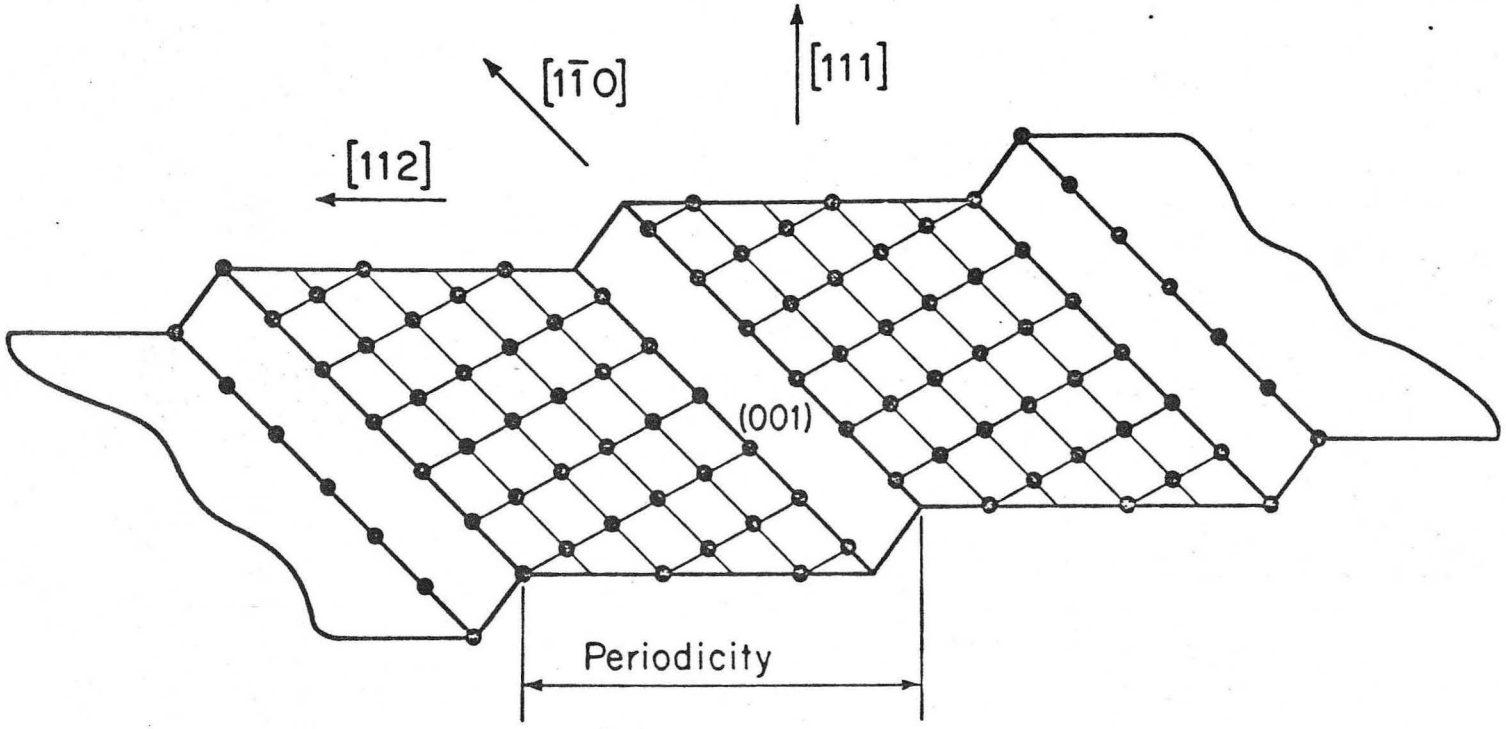
XBB 719-4595

Fig. 2c



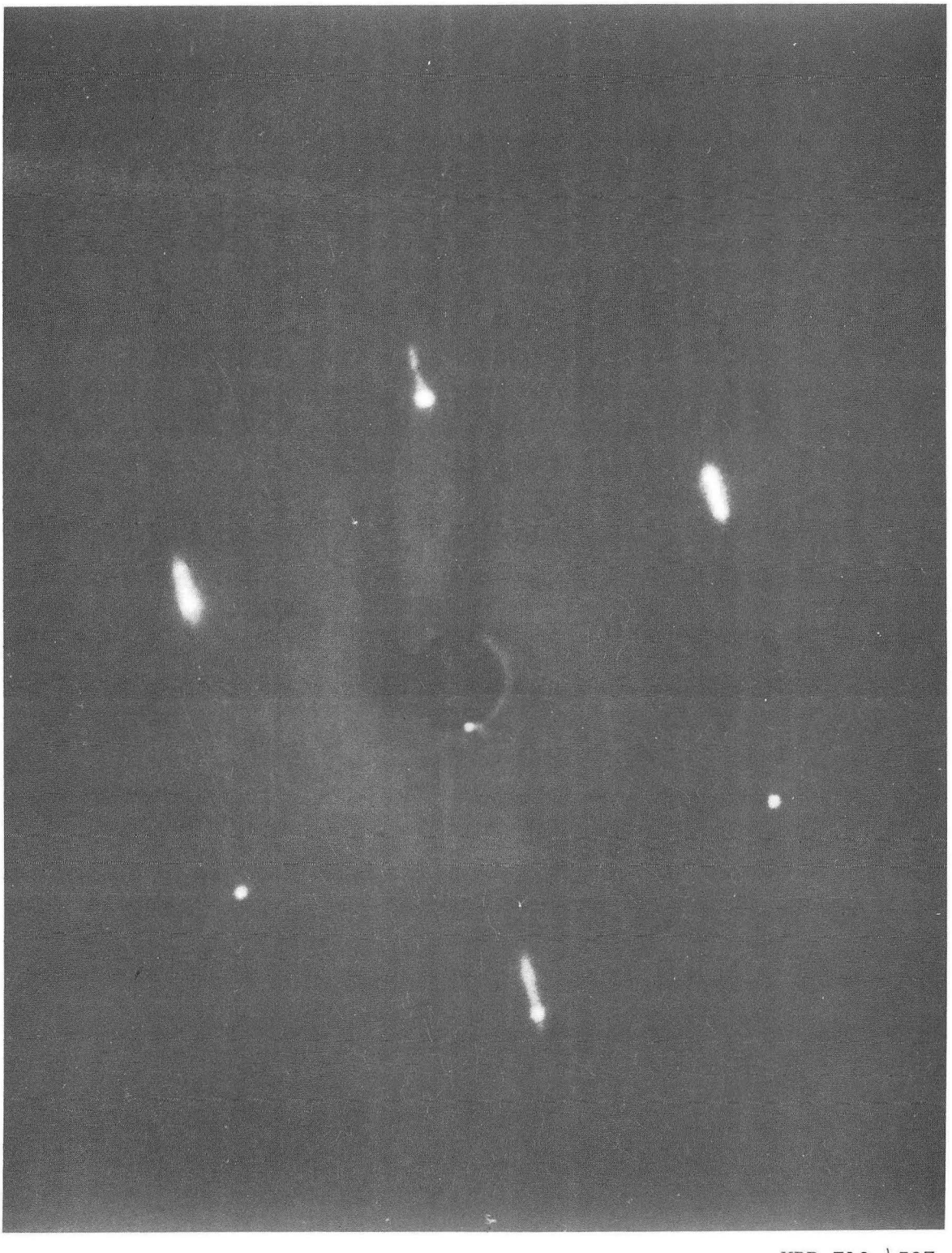
XBL 716-6802

Fig. 3a



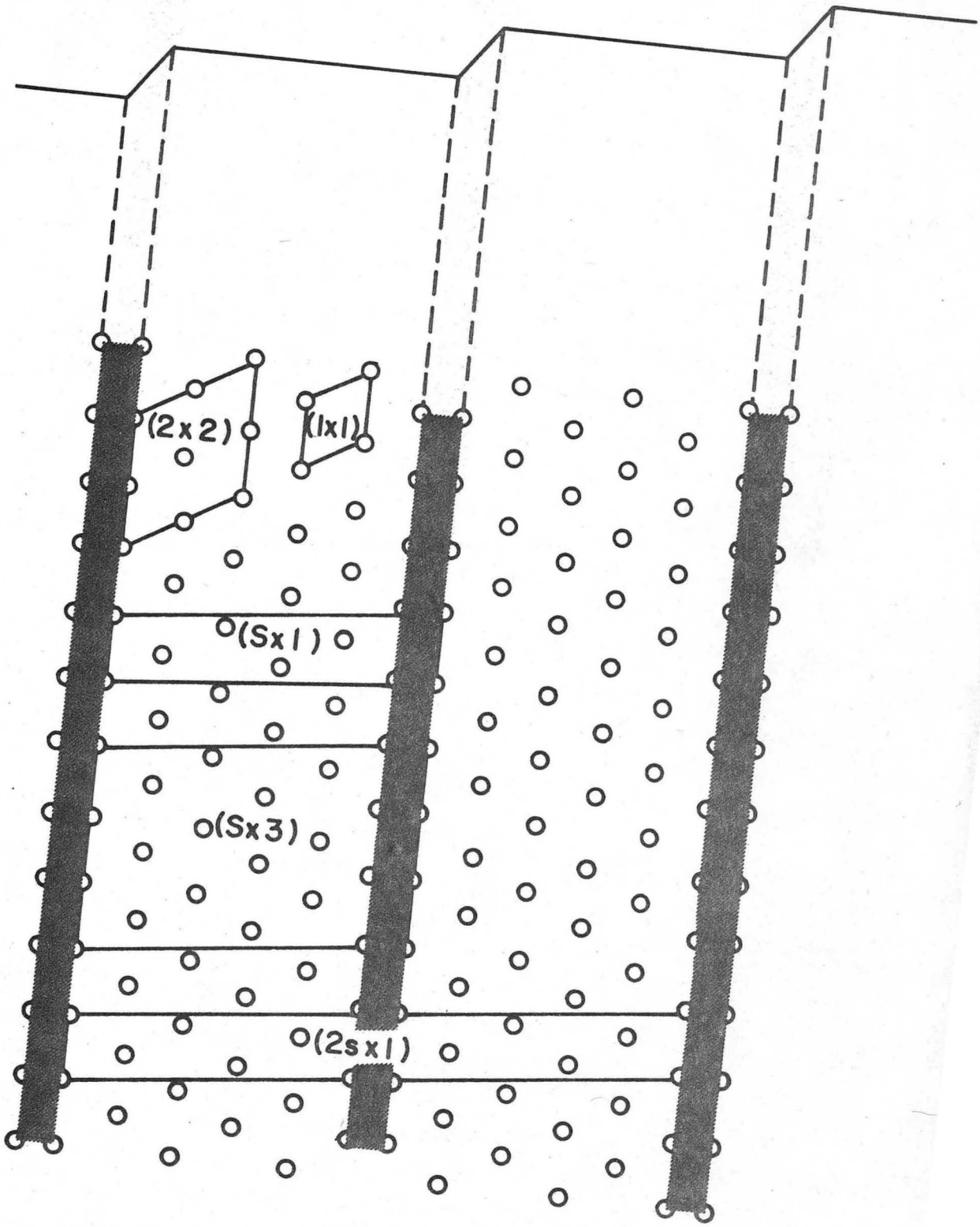
XBL 716-6801

Fig. 3b



XBB 719-4597

Fig. 4



XBL7110-4466

Fig. 5

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