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The technique of low energy electron diffraction has developed into a reliable means of studying the structure of solid surfaces and chemical surface reactions of particular interest to metallurgists.

INTRODUCTION

Investigations of the chemical and physical properties of surfaces not only have great practical importance, but are equally fascinating and exciting from a purely scientific point of view. In fact, one could look upon the surface region as a separate and distinct two dimensional phase which can undergo phase transformations similar to those of the bulk (for example order-disorder transitions, structural rearragements, etc.[1]) Until recently, however, the surface of a solid has been characterized primarily by measurements of macroscopic properties such as contact angles, adsorption isotherms, etc. Unfortunately, such measurements do not provide information on the atomic processes taking place at the surface. A complete understanding of these physical-chemical processes requires a study on an atomic scale of well-defined single crystal surfaces under controlled conditions, i.e., ultra high vacuum, ($< 10^{-8}$ torr) and/or in an ambient of pure gases.

Several experimental techniques can be used to investigate the surface in this manner; perhaps the most prominent are field-emission, field-ion microscopy and low energy electron diffraction. There are experimental limitations on the applicability of each and one alone cannot furnish complete information on all of the properties of surfaces. Field-ion and field-emission microscopy are primarily used to study the surface properties of metals and have been well described in the literature.[2,3] Low energy electron diffraction (LEED) can be used on any crystalline material (metal, semiconductors, insulators) and is easily combined with many other techniques such as mass spectroscopy, work function measurements, etc. It is our primary source of information

on the structural arrangement of surface atoms and can also be used to study the chemical reactions which take place at the interface. In addition, nucleation, epitaxy, thin film growth, and surface diffusion which are processes of fundamental importance in material science can be conveniently studied by low energy electron diffraction also.

At the present time, however, the technique of LEED is not well known to the practising metallurgist. Therefore, the purpose of this paper is to describe the technique (both experimental and theoretical), review its application to the studies of pure metal and alloy surfaces, and to point out its usefulness to the study of a variety of surface processes of great technical interest. We believe that LEED promises to become a basic tool in material science laboratories, and it is hoped that this article will stimulate increased activity by metallurgists in this important field of science.

THE METHOD OF LOW ENERGY ELECTRON DIFFRACTION

The experimental technique of low energy electron diffraction has developed since the early work of Davisson and Germer[4] to such an extent that commercial apparatuses are now available. Farnsworth[5] was, perhaps, the first to explore its applicability to surface studies; and his work stimulated increased activity in the field. Germer et al.[6] improved an earlier design by Ehrenberg[7] and perfected the post acceleration or display-type apparatus. The rapid development of high vacuum technology and the availability of high purity single crystals makes the experiment rather simple once the capabilities and limitations of the apparatus are clearly understood. A schematic of the diffraction chamber of the display type is shown in Fig. 1. Only the essential features of the diffraction equipment will be described since all the important details of each component along with improvements in design are described in the literature.[8]

A monochromatic beam of electrons (approximately 1 mm^2 in cross-sectional area) is electrostatically focused onto the sample (S) which is maintained at the center of curvature of the fluorescent screen (F). The low penetrating power of these electrons which have energies from a few to 500 electron volts (eV) and the magnitude of the associated wavelengths, (.5 - 5Å) [$\lambda = \sqrt{150/V}$, where V (beam voltage) is in volts] are well suited to the investigation of surface structure. The sample and the first grid (G_1) are maintained at ground potential. The region between them is then field free and the path of the impinging and back reflected electrons is not distorted. The inelastically scattered electrons, i.e., electrons which have lost energy due to interaction with the surface, are repelled by the second grid (G_2) which is

generally maintained at cathode potential. Only the elastically scattered electrons are of sufficient energy to penetrate the second grid (G_2). These electrons are then accelerated to a hemispherical fluorescent screen (+5 kV) where the diffraction pattern which corresponds to the surface structure is displayed. The fraction of elastically scattered electrons decreases with increasing electron energy and will depend on the material studied. It is approximately 5-10% of the total in the 100-450 eV range, but 50-80% at 20 eV. Therefore the surface is most reflective for low energy electrons. The diffraction pattern can be viewed and photographed through the window (W) at the front of the diffraction chamber which is part of a vacuum system quite capable of pressures in the 10^{-10} - 10^{-9} torr range. The crystal is maintained under ultra high vacuum to avoid possible contamination of the surface by the adsorption of gases from the ambient. The adsorption of most gases on the crystal surface will result in monolayer coverage within seconds* at 10^{-6} torr. However, ultra high vacuum conditions allows for reasonable observation times of a clean sample. The crystal (S) can be rotated and undergo both horizontal or vertical motion. Furthermore, the crystal can be heated by resistance heating, thermal conduction or electron bombardment. Cooling to liquid nitrogen temperatures is also possible with a specially designed sample holder.

The intensity of any diffraction spots and any variation in intensity due to adsorption, changes in electron energy, crystal orientation and temperature can be accurately measured by a spot photometer. This is only a relative measurement as compared to the Faraday cup method[5] which measures the total electron flux and therefore the absolute intensity.

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* This is only true for a sticking probability of unity.

III. THE NATURE OF LOW ENERGY ELECTRON DIFFRACTION

The conditions for the diffraction of an electron or x-ray beam of suitable wavelength ($\lambda \leq d$) from a single row of equally spaced atoms is shown in Fig. 2a. Diffraction results from the constructive interference of the scattered waves (rays A and B). This occurs when the path difference ($d \cos \theta$) between rays A and B is an integral number of wavelengths ($m\lambda$) and is expressed by the equation,

$$d \cos \theta = m\lambda \tag{1}$$

Diffraction by two mutually perpendicular rows of atoms, i.e., a two-dimensional lattice plane occurs when there is constructive interference of the scattered waves from the parallel rows. This is shown in Fig. 2b. The condition of the two-dimensional diffraction can be expressed by

$$d_{hk} \cos \theta_{hk} = m\sqrt{150/V} \tag{2}$$

where d_{hk} is the spacing between any two parallel rows in the surface grating which can be designated by Miller indices (hk). θ_{hk} is the scattering angle.* The locus of this constructive interference between the diffracted waves is a set of parallel lines or rods which are perpendicular to the lattice plane. Therefore, two-dimensional diffraction results in spots at the intersection of these "rods" with the fluorescent screen. The diffraction pattern should be observable at all wavelengths smaller than d_{hk}.

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* Note that the scattering angle is a function of the wavelength of the incident electrons according to Eq. (2).

If the electron beam penetrates below the first surface plane diffraction will occur due to the constructive interference between the scattered waves from the first plane and from planes below. Such constructive interference occurs when

$$2z \sin \theta = m\lambda \qquad (3)$$

where z is the distance between planes as shown in Fig. 2c. Thus, the conditions for diffraction by a three-dimensional solid are stricter than for the diffraction by a lattice plane (Eq. 2) and are met only at well defined electron wavelengths (Bragg condition).

The case encountered by LEED is therefore intermediate between two- and three-dimensional diffraction. At low electron energies (< 50 eV) the largest fraction of the diffracted electrons back-scatter from the surface plane. As the electron energy increases, a larger fraction of the impinging electrons penetrate a few atomic planes below the surface and the three-dimensional character of low energy electron diffraction becomes more pronounced. The penetration depth, the ratio of electrons which are back scattered from the surface to those from atomic planes below the surface at a given electron energy, is a function of the crystal potential that the electron encounters upon approaching the solid. Electrons are scattered by this potential; whereas x-rays are scattered by the electrons surrounding the nuclei of the solid. Therefore, hydrogen atoms can be just as effective in the scattering of electrons as much heavier elements which contain many more electrons. Furthermore the charge, large mass and low energy of the electrons compared to electromagnetic waves of comparable wavelength make low energy electrons ideal for surface studies. Their "scattering amplitude" which is a measure of their scattering

probability is several orders of magnitude higher (≈ 1 Å) than for x-rays. This is the reason for the observed high intensity diffraction patterns which can be obtained from ordered structures composed of no more than 5-10% of the total number of surface atoms.[1]

The crystallography of two-dimensional structures, related symmetry operations and special conventions have been outlined by Wood.[9] The arrangement of surface atoms which is identical to that in the bulk unit cell is called the "substrate" structure and is designated by (1 × 1). For example, the (100) "substrate" structure of platinum is designated Pt(100) - (1 × 1). The corresponding diffraction pattern for the (100) face centered cubic lattice is shown in Fig. 3A. Any other arrangement of surface atoms is called the "surface net" or "surface structure." When the unit cell of the surface structure is twice as long as the bulk unit cell along one crystallographic direction and the same length along the other direction, it is designated (2 × 1). The corresponding diffraction pattern for a (100) FCC crystal is shown in Fig. 3B. The (2 × 2) and (5 × 1) surface structures are represented in Fig. 3C and 3D.

If an adsorbed gas forms a (2 × 1) surface structure such as oxygen on the (110) face of nickel,[10] it is designated Ni(110) - (2 × 1) - O. If the unit cell of this surface structure is rotated by 45° with respect to the substrate unit cell, it could be designated by Ni(110) - (2 × 1) - 45° -O.

INTENSITY CONSIDERATIONS

The diffraction pattern is representative of the arrangements of atoms on the surface. However, an intensity analysis of the diffraction features is necessary for a rigorous understanding of the scattering mechanism and to distinguish between several structures which could yield similar diffraction patterns. Although structure analysis cannot yet be carried out, recent contributions by Heine[11] and McRae[12] and others to the theory of low energy electron diffraction indicate that the formulation of a working model for structural computations is imminent. We shall only present here some of the considerations which have played an important part in the theoretical development of low energy electron diffraction phenomena.

In the kinematical theory of scattering, the intensity of the scattered waves is assumed small compared to the intensity of the incident beam and therefore multiple beam interactions are neglected. In light of the large scattering amplitudes of low energy electrons with respect to that of x-rays the applicability of the kinematic approximation in LEED studies has to be carefully examined. It is likely to be applicable in the intermediate and high electron energy range when absorption factors are large and back-scattering amplitudes small. At lower electron energies (< 50 eV) the intensity of the elastically scattered electron beam is high and multiple beam interactions may have to be taken into account. For this case, the dynamical theory of diffraction should be applied.

The interaction between the incident electrons and the potential field of the atoms within the surface region of the crystalline sample is described by the atomic scattering factor (f). The atomic

scattering factor is a function of the wavelength and scattering angle. The distribution of the scattering centers in the unit cell of the surface will determine the amplitude of the resultant wave scattered by all the centers of the unit cell. The structure factor (F) uniquely describes both the amplitude and phase of this resultant wave with intensity proportional to F^2. Theoretical expressions for F have appeared in the literature,[1,13] but interpretation of the diffracted intensities in terms of a suitable theory has yet to be developed. One outstanding drawback is the lack of accurate atomic scattering factors (f) for low energy electron scattering by surface atoms.

A typical plot of the intensity dependence of the specular reflection (00) on the energy of the incident electrons, I_{00} vs V, is shown in Fig. 4. The intensity spectrum goes through a continuous series of maxima and minima. Some of the maxima can be associated with the Bragg condition of diffraction (Eq. 3). The calculated values of the positions of these maxima are shifted with respect to the experimental values due to the energy increase of the incident electrons as they enter the crystal from the vacuum. This is referred to as the inner potential of the crystal (V_o) and its value is roughly between 5-30 eV for the different solids. Equation (3) should then be written as

$$m\lambda = 2z \sin \theta = m \sqrt{150/(V+V_o)} \qquad (4)$$

In addition to Bragg peaks, the presence of many additional peaks is apparent in the electron energy range of interest. Some of these are identified as "secondary Bragg peaks" and are believed to be due to the asymmetry of the environment of surface atoms (i.e., electron density

distribution, mean displacements, etc.) as compared to atoms in the bulk of the crystal.

The appearance of these secondary Bragg peaks (Fig. 4) in the intensity curves seems to be a general feature of low energy electron diffraction. Adsorbed gases can often cause these peaks to disappear or greatly reduce their intensity. This effect was independent of the particular adsorbate (nitrogen, oxygen, carbon) for the (100) face of tungsten.[14] Therefore, it should not be due to the configuration[15] or scattering[16] properties of the adsorbed layer, but may be caused by an abrupt change in the periodicity of the scattering potential. Other peaks could be due to intensity sharing between different order diffracted beams and to surface steps.

Measurements of I_{00} vs V as the orientation of the single crystal is varied with respect to the incident beam are very useful since any theory of low energy electron diffraction must take the orientation of the single crystal into consideration also. Furthermore, the effect of lower planes on the scattered intensity will be a function of the orientation of the sample and is greatest at the smaller angles of incidence. Monitoring the intensity change of other diffraction spots (I_{10}, I_{11}, etc. vs V) is complicated by the fact that their mean position (the scattering angle at which they appear) is not constant with beam voltage. The position of the (00) spot (specular reflection) will remain constant with beam voltage.

The intensities of the back-diffracted electron beams decrease rapidly with increasing temperature, and the measurement of the temperature dependence of the diffracted beam intensity (Debye-Waller factor) can be used to determine the root mean displacement of surface atoms. Such experiments have been carried out and will be discussed in the section on clean metal surface studies.

SURFACE PREPARATION

Surface preparation of the single crystal sample is crucial to the success of low energy electron diffraction experiments. The quality of the diffraction pattern will depend on the size and number of domains on the surface with well defined periodicity and on the cleanliness of the crystal. Therefore, the single crystal which is to be used in the study must be cut, oriented, polished and/or etched carefully. Careless cutting and polishing will introduce local strain, contaminants and can result in the formation of an amorphous surface layer as much as 10^{-4} - 10^{-3} cm thick. This damaged layer must be removed before the crystal surface becomes suitable for low energy electron diffraction studies. The orientation of the crystal [(100), etc.] should be within 1° of the chosen crystal face if possible. When convenient, vacuum cleavage techniques can eliminate some of the difficulties of surface preparation. However, most metals are difficult to cleave, especially under vacuum; they are usually mechanically or electrochemically polished and etched. Surface damage or surface contaminants can be removed by xenon or argon ion bombardments of the sample in the diffraction chamber at pressures of about 10^{-5} torr and ion beam energies in the 140-340 eV range. The effect of ion bombardment on solid surfaces has been discussed in several recent papers.[17,18] Any surface damage introduced by ion bombardment can usually be removed by high temperature annealing. Subsequent quenching or slow cooling of the crystal is dependent upon the geometry and size of the crystal holder and on the crystal's geometry. High temperature structural arrangements may or may not remain after a slow cool; while quenching may result in an ordered structure. Slow cooling may be controlled by programming the resistance

heating by decreasing current flow as a function of time. An additional difficulty in surface preparation is the possibility of the diffusion of impurities from the bulk which along with the sample holders is a source of surface contaminants. Such diffusion is enhanced at high temperatures.

Since the low energy electrons are excellent scatterers, less than a monolayer of an ordered adsorbed layer is detectable and often leads to extra diffraction features which can complicate or interfere with the experiment. Therefore the ambient of the ultra-high vacuum diffraction chamber should be monitored by a mass spectrometer and any extra features in the observed diffraction pattern correlated to the observed mass spectrum. The reactivity of the particular metal studied for any of these gaseous contaminants and the solubility of different contaminants in the metal are very important considerations in the final analysis of results. Dominant residual gases in the diffraction chamber at 10^{-9} torr are carbon monoxide, water vapor, hydrogen and argon. The carbon monoxide could be produced by the degassing of the vac-ion pump, or by the hot tungsten filament used to produce the beam of electrons for ion bombardment. Argon is used for ion bombardment and can also come from the pump. The presence of hydrogen and water vapor probably comes from the stainless steel walls of the chamber. Several bakings of the diffraction chamber will help to eliminate or greatly reduce the presence of water vapor and a helium cold finger can also be used to remove these gaseous contaminants. Furthermore, the recent development of secondary electron spectroscopy[19] (Auger electron emission) which can detect and identify very small concentrations of surface impurities should aid in the characterization of the solid surfaces used in LEED studies.

LEED STUDIES ON CLEAN METALS

The exact meaning of a "clean" surface must depend on the limits of impurity detection. This detection limit is obviously a function of the experimental technique used. In low energy electron diffraction, detection is limited to ordered domains on the surface which are much smaller than the electron beam size (1 mm^2) and contains approximately 10^{12} surface atoms. A surface with a concentration of ordered impurities below this limit (less than $10^{12}/cm^2$ impurities) can be defined as "clean" within the experimental limitations of LEED. Therefore the term "clean" will be used for a surface displaying no extra diffraction features which are caused by the presence of ordered impurities. The reproducibility of extra diffraction features on a "clean" surface from sample to sample and by different research groups should imply that within the capabilities of the experimental technique the surface is free of gross contamination (i.e., amorphous adsorbed layers, etc.). However, the effects of gases, changes in beam voltage, temperature, etc. on the "clean" diffraction pattern must be carefully studied before any definite conclusions concerning the arrangement of atoms on the "clean" surface are made. One should use techniques such as mass spectroscopy, secondary electron spectroscopy, etc. in conjunction with these experiments, in an effort to make the results obtained by LEED even more meaningful and reliable.

An exciting discovery by LEED has been that surface atoms may be arranged in surface structures with different translational symmetry than that of the bulk atoms. Surface structures which have been attributed to the clean surface have been observed on semiconductor (Si,[20] Ge,[20] etc.) metal

(Pt,[21] Au,[22,23,24] Pd,[22] Ag,[22] etc.) and insulator (Al_2O_3)[25] samples. For these solids the surface structure ordered or disordered appear in well defined temperature ranges. A list of the surface structures which were detected on clean metal surfaces and their approximate range of stability is shown in Table I.

After several years of concerted studies in different laboratories and considerable debate the presence of these surface phase transformations on semiconductor surfaces have been well accepted and attributed to ordered rearrangements of the surface atoms of the clean solid. Due to the more recent discovery of surface structures on clean metal surfaces there is still debate on the nature of these rearrangements. Somorjai et al.[21,22] presented experimental evidence which indicates that the observed phase transformations are indeed the properties of the clean metal surfaces. Fedak and Gjostein[23] on the other hand feel that the same diffraction features on gold surfaces are due to unspecified surface contaminants. Palmberg and Rhodin[24] presented further evidence in support of the clean metal surface structure model when they formed the Au(100)-(5×1) surface structure by epitaxially depositing gold onto several ionic single crystal substrates (MgO and KCl). Additional experiments evidence supporting the fact that the surface structures observed are due to the clean gold surface has been summarized in a recent note.[26]

Atoms at the surface of a crystal are in a different environment than those in the bulk - they are surrounded by smaller numbers of nearest neighbors. It is to be expected then that the mean square displacements of surface atoms are different from atoms in the bulk of the crystal.

Table I.

Surface structures on the substrates of gold, platinum, silver, palladium, antimony, and bismuth and their approximate temperature ranges of stability.

Substrate	Surface Structures	Approximate Temperature range (°C)
Au(100)[22,23,24]	(5x1)	25-400
	(6x6)	350-550
	ring (⊙)	> 750
Au(110)[23]	(2x1)	800
Pt(100)[21]	(2x1)	300-500
	(5x1)	350-500
	ring (⊙)	> 600
Pt(110)[21]	(⊙)[a]	> 600
Pt(111)[21]	(2x2)	800-1000
	(3x3)	800-1000
	(⊙)[a]	> 900
Ag(100)[22]	c(2x2)	600-750
	ring (⊙)	> 750
Pd(100)[22]	(2x1)	200-300
	(2x2)	250-550
	c(2x2)	> 550
Sb(11$\bar{2}$0)[38]	(6x3)	> 25
Bi(11$\bar{2}$0)[38]	(2x10)	> 25

[a] The notation ⊙ indicates a ringlike diffraction pattern.

Measurement of the temperature dependence of the intensity of the (00)-reflection (Debye-Waller factor) allows one to calculate the root mean square displacements normal to the surface planes, $\langle \mu_{\perp} \rangle$. The mean square displacement, $\langle \mu_{\perp} \rangle$, for the surface atoms of face centered cubic metals are greater than those in the bulk.[27,28,29] Low energy electron diffraction seems to be the only experimental tool sufficiently sensitive to detect this effect. In addition, the surface Debye temperatures have also been calculated for these face centered cubic metals.

Studies on the clean surfaces of nickel,[10] copper,[30] tungsten,[31] silver[25] (111), chromium,[32] titanium,[33] niobium,[34] tantalum,[34] vanadium,[34] iron,[35] aluminum,[36] and molybdenum,[37] antimony,[38] bismuth[38*] has not revealed the formation of surface structures. The surface atoms of these metals (at least for the studied crystal orientation) have the same unit cell as that of the bulk.

Experimental results using nickel surfaces have been interpreted as indicating a larger net displacement between the first two atomic planes.[10] However, Park and Farnsworth[39] used an electrical method of detection (Faraday cage) to study the variation of the intensity of the diffraction spots with temperature and found no net displacement within an experimental error of about two percent. More experimental and theoretical work will help to resolve this exciting problem.

LEED continues to provide information on the surface properties of clean metals. This information is essential for work in epitaxy and

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* The $\{11\bar{2}0\}$ surfaces of antimony and bismuth undergo surface reconstruction.

heterogeneous catalysis. In order to understand the exact nature of the adsorption process, the arrangement of atoms on the clean surface and its temperature stability must be determined.

LEED OBSERVATIONS ON CORROSION DUE TO OXIDATION AND THE ADSORPTION OF GASES BY METALS

Corrosion due to oxidation is common and results in the deterioration of many metals. A typical example is the rusting of iron due to the presence of oxygen and water vapor. In order to minimize the possibility of its occurence, the metallurgist should understand the detailed mechanism of the chemical reaction leading to corrosion and provide protection against it. The adsorption of oxygen on several metals of various crystallographic orientations (Ni,[10] Pt,[40] Cu,[30] Rh,[41] W,[31] Mo,[37] Ta,[42] Cr,[32] Fe[35]) has been studied by low energy electron diffraction. The adsorption rates were found to be strongly dependent on the oxygen exposure time and on the temperature of the sample during this exposure. A most significant observation by LEED has been that the adsorbed oxygen can form ordered structures on the surface of the metal. The amount of gas adsorbed, its arrangement and composition on the surface, and the accommodation coefficient of the oxygen was found to be strongly dependent on the crystallographic orientation of the surface.

The concentration of surface steps and facets is expected to affect the reaction rate of oxygen on the metal surface. Therefore, results of gas-solid interactions must be interpreted with consideration to the surface preparation (i.e., chemical etching and/or electropolishing, ion bombardment, gas exposure times, etc.) of the sample. Discrepancies between various investigations can often be attributed to subtle differences in surface treatments, but their exact effect on gas-metal interactions is not known with certainty at the present time. Nevertheless,

the appearance of extra features in the normal diffraction pattern and a knowledge of their beam voltage and temperature dependence has provided reliable evidence for one-, two- and three-dimensional ordered structures as adsorption takes place on the surface. Most of the surface structures observed have exhibited a finite rate of formation which was a function of the experimental conditions (temperature, gas pressure • time product, crystallographic orientation). Therefore the appearance of extra diffraction features is not spontaneous, but seems to be associated with the ordering of a surface phase.

Chang and Germer[43] found for the (112) face of tungsten that the intensity of the extra (h + 1/2k) spots was a function of the pressure - time (torr • sec) product of the oxygen exposure. When the (h + 1/2k) spots are at a maximum intensity the surface structure corresponds to the presence of approximately half a monolayer of oxygen. For the initial adsorption of oxygen on (110) copper,[30] streaks attributed to the random adsorption of oxygen in the troughs of the (110) surface were observed. Upon further exposure, the streaks collapsed into extra spots which was taken as evidence for the ordering of the surface structure. The transition of this structure into a second structure was also observed. A study of the oxidation[44] of (111) nickel revealed that nickel oxide formed with the (100) surface exposed and with its (111) plane parallel to the surface plane of the metal. The diffusiveness of the extra diffraction spots was related to the size of the nickel oxide crystallites (approximately 30 Å). These results demonstrate the usefulness of LEED in nucleation and two-dimensional transformation studies also. Prior to this work little was known about the initial nucleation process and the

prevalence and importance of ordered intermediate surface structures as evidenced by the extra features of the diffraction pattern.

A variety of structural arrangements can be postulated to interpret the extra features of the diffraction pattern due to the uptake of oxygen. For example, one interpretation of the results on the oxidation of the (110) face of nickel[10] and copper[30] is that these surfaces actually undergo reconstruction during oxygen adsorption. The metal surface atoms migrate to new surface sites and the resulting adsorption layer consists of both oxygen and metal atoms. Arguments for[45] and against[46] such a possibility have appeared in the literature. Once a theoretical foundation for an analysis of the diffracted beam intensities is established such differences in interpretation will be resolved.

Lander[47] and Estrup and Anderson[14] have discussed the contribution of LEED to our knowledge of chemisorption and the discovery of ordered surface structures. A recent LEED study on chromium[32] surfaces points out that the probable reason for the non-corrosive character of chromium is the presence of a strongly bound amorphous oxide surface layer. The LEED study of the oxidation of clean (100) face of iron[35] has particular significance to metallurgists and shows that FeO is formed as expected. The surface of iron is very difficult to clean. Its surface is contaminated with carbon and it undergoes a phase transition (BCC $\rightarrow$ FCC) above 900°C.

The adsorption of other gases (N_2, H_2, CO, CO_2, etc.) on metals continues to be studied by LEED also. A large variety of ordered structures has been observed.[1,48,49] The interactions of these gases with metal or alloys has often been put to a useful purpose by the metallurgist. The

case hardening of some steels by nitrogen and carbonaceous atmospheres are well known examples. In addition, information on the interactions of a mixture[50] of these gases on metal surfaces has also been obtained.

The interaction of gases with metals and alloys are an important field of study for the metallurgist. Gases are initially adsorbed at the surface and can diffuse into the bulk of the metal (solubility). Well known examples are the steam embrittlement of copper containing oxygen in a hydrogen atmosphere and the embrittlement of zirconium and titanium by hydrogen. A detailed study of the selective oxidation of the most active component of an alloy is also of practical interest to the metallurgist. In the case of copper-nickel alloys, the selective oxidation of the nickel reduces the resistance of the alloy and results in a higher electrical conductivity. Another interesting problem is that iron will not absorb nitrogen in any appreciable quantity below 900°C, but if a small percentage of hydrogen is added the equilibrium between the metal and nitrogen is more rapidly established. Although the thermodynamics[51] of this phenomena have been studied, the detailed microscopic processes are unknown.

We have mentioned only a few outstanding metallurgical problems which can be successfully studied by LEED. No doubt the reader can add to this list. Many of these problems will be studied in the near future* and the availability of alloys in single crystal form will eventually result in a much greater understanding of the surface properties of alloys which have yet to be studied on an atomic scale.

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* G. W. Simmons of the engineering experimental station at Georgia Tech is beginning a study of stainless steel (austenitic single crystal) in a corrosive atmosphere with a LEED apparatus modified by Varian Inc.

LEED STUDIES ON EPITAXY, THIN FILM GROWTH, ALLOY FORMATION

Metals deposited from the vapor onto a single crystal substrate are commonly found to be crystallographically oriented ("epitaxy"). These epitaxial layers have important applications as components in many solid state circuits. Detailed information on the structural arrangements of metals deposited onto metal substrates is also important because of their application in such fields as thermionics, protective coatings, composites, etc. Past research has shown that both the nature and degree of the thin film's orientation was dependent upon the crystallographic orientation and temperature of the substrate during deposition as well as on the properties of the condensing metal itself. The orientation, degree of order, and structural transformations of the deposited metal from fractional to multilayer coverage can be successfully studied by LEED. The work by LEED has not only verified the results of past research, but has contributed to a more detailed understanding of the nature of epitaxy.

Just as in the case of the adsorption of noncondensible gases, deposited metals can also form ordered surface structures. These structures can undergo further rearrangements during continued condensation. More significantly, the structural properties of the epitaxial deposits are strongly dependent on the structure of the clean substrate surface. Cesium, tin, lead, aluminum, indium, phosphorous, calcium, and barium have been deposited on the cleaved (111) face of silicon single crystals. General trends in the results have been summarized by Lander.[1] Three ordered phases with successive additions of cesium[52] were observed to form. In the presence of the (7x7) surface structure which is one of the ordered surface phases of the clean silicon (111) crystal face no ordering of the

condensed cesium could be detected. The other metals, however, formed well ordered structures on both the Si (111) and the Si (111)-(7×7) surfaces and showed order-disorder transitions in well-defined temperature ranges. The epitaxial deposition of silicon vapor on the (111) silicon substrate was also found[53] to be sensitive to the presence of silicon surface structures.

The copper-titanium,[54] copper-tungsten,[55] nickel-copper,[56] thorium-tungsten[57] systems have been studied by LEED. There was a pronounced effect of chemisorbed oxygen on the orientation of the Cu-Ti (001) and Cu-W (110) systems. In the Cu-Ti (001) system, the deposited copper formed as discrete oriented crystallites on clean titanium, but was disordered on a surface covered with a chemisorbed layer of oxygen. The epitaxy of copper on tungsten (110) was severely inhibited by the chemisorption of oxygen also. These observations indicate that epitaxial growth must be performed under ultrahigh vacuum conditions in order to maintain reproducible film properties. For the Ni-Cu (111) system the interatomic distance in the thin nickel film did not seem to be effected by the difference in the lattice spacing of the substrate and that of the deposited metal. Taylor[55] reported the appearance of a long-period superlattice "alloy" diffraction pattern which resulted when the tungsten substrate was heated after the deposition of copper. He proposed that this pattern was due to the formation of a tungsten-copper alloy. Secondary electron spectroscopy may be very useful in determining the composition and structure of these surface alloys formed in epitaxial studies.[19] The epitaxy of metals (Au, Ag) on ionic substrates (MgO and KCl) has also been investigated.[24]

Epitaxial studies were also found to be useful in estimating the number of atomic layers which actually contribute to the scattered intensity in the LEED diffraction pattern. Haque and Farnsworth[54] found for the Ni-Cu (111) system that at 250 volts only the atoms in the first three layers were contributing to the scattered intensity observed. Below about 150 volts, only the first two atomic layers were contributing. The number of studies of epitaxy by LEED has greatly increased in the last three years and continues to be of great practical interest.

SURFACE SELF DIFFUSION

Surface self diffusion rates are sensitive[58] to the structure of the surface and can be conveniently studied by LEED. This information is essential for a clear understanding of the atomic migration of surface atoms and the elementary steps of surface reactions.

Bombardment of the metal single crystal surface by high energy noble gas ions is often necessary prior to the LEED experiment. However, the surface of the metal can be disordered due to this bombardment and a large concentration of adsorbed, absorbed (solubility) gaseous atoms, and metal ad-atoms can result. After bombardment the intensity of the diffraction spots diminish. In fact, spots visible at low voltage prior to bombardment often disappear after prolonged bombardment. High temperature annealing of the sample tends to reorder the disordered surface as a result of the increased motion of the metal ad-atoms and causes the desorption of the adsorbed gaseous atoms. The effect of high temperature annealing on the diffusion rates of the metal ad-atoms can be monitored by following the intensity increase of the diffracted spots as a function of time at different annealing temperatures which is related to the self-diffusion of the metal ad-atoms. The effect of desorption on the intensity change could then be determined since the desorption can be monitored with a mass-spectrometer. Studies of this kind have not been carried out as of yet. However, the kinetics of the formation of the (5x1) surface structure on Pt[21] has been studied in this way by monitoring the change in intensity of the extra diffraction features. The activation energy of formation found (≈ 38 kcal/mole) was roughly half of that for the self-diffusion of platinum atoms in the bulk crystal. This is reasonable magnitude since the (5x1) is believed

to be due to the rearrangement of the platinum atoms on the surface. In addition, Bonzel and Gjostein[59] have measured the surface self-diffusion of copper by means of a laser diffraction pattern while studying the structure of the surface with LEED.

Undoubtedly LEED will play an increased role in the study of surface diffusion phenomenon on clean surfaces and its relationship to the structure of the surface.

SUMMARY

The technique of low energy electron diffraction has contributed tremendously to our increasing knowledge of surface phenomena. During the past several years it has proven to be an invaluable tool for the study of surface properties. It has revealed that clean solid surfaces can undergo structural rearrangements at temperatures where there is no apparent change in the bulk crystal structure and that the adsorption and reaction of gases may proceed via several ordered intermediate surface structures. In addition, the investigations of clean metal surfaces and the reactions which take place upon them such as oxidation, epitaxy, thin-film growth, etc., have yielded information on surface processes which could not have been obtained by any other technique. These include surface phase transformations, possible reconstruction of the surface atoms in the presence of adsorbed gases, the periodic nature of the adsorbed atoms and the sensitivity of epitaxial growth to the presence of chemisorbed gases. Such results have scientific as well as practical importance and are especially interesting to the metallurgist.

The technique continues to develop and is often used in conjunction with other measurements such as mass spectroscopy, work function studies, etc. Once a reliable theoretical foundation for the analysis of intensity data is established, the role of low energy electron diffraction (LEED) in surface studies will be similar to that of x-ray diffraction in studies of the solid state.

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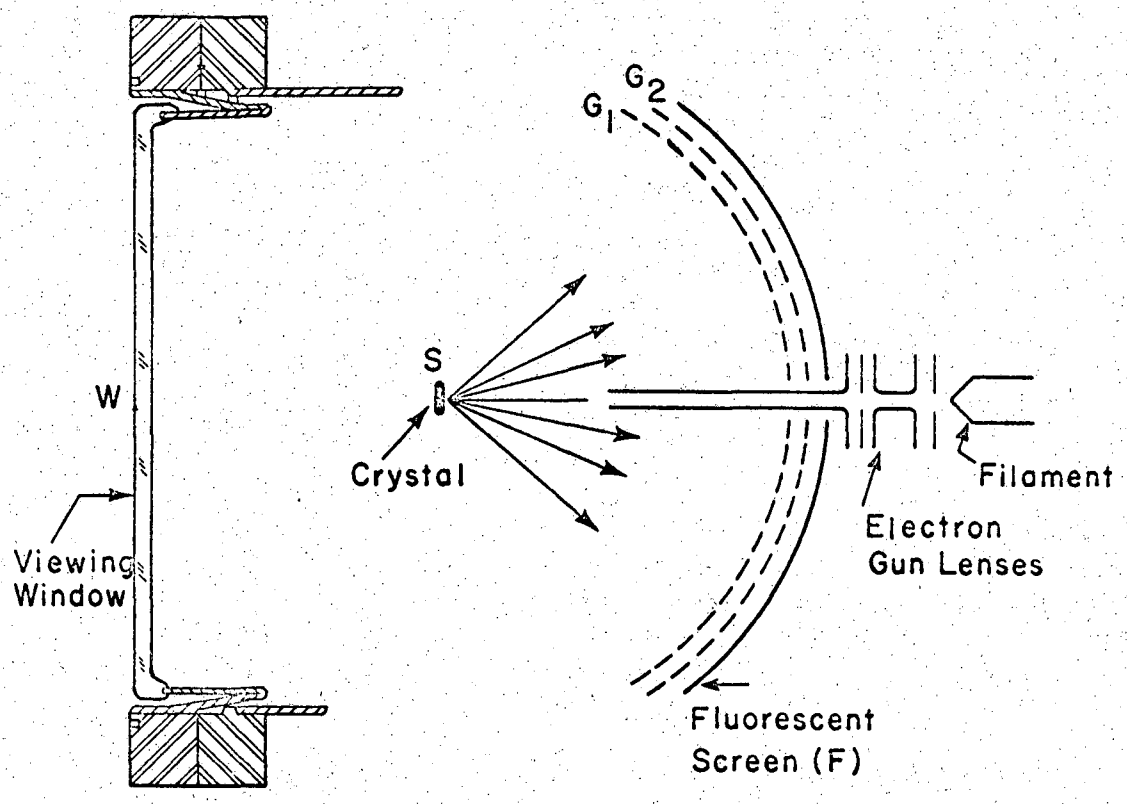

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Fig. 1 Low energy electron diffraction chamber.

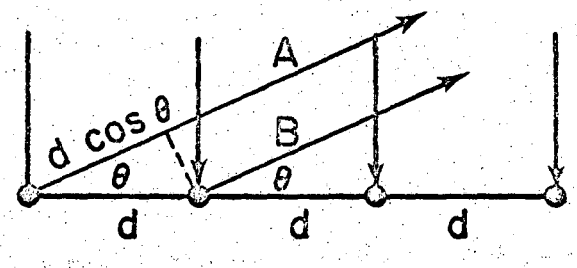

Fig. 2a Diffraction for normal incidence from a single row of atoms which are d apart.

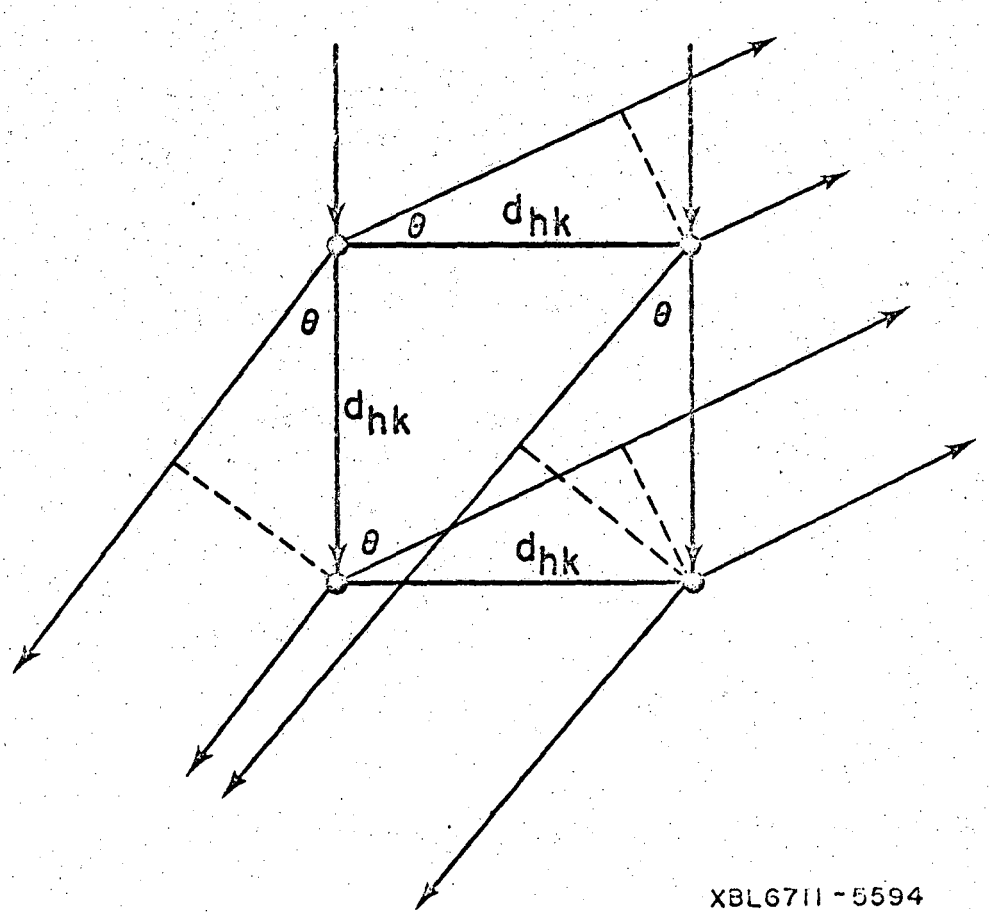

Fig. 2b Two dimensional diffraction from the lattice plane for normal incidence. θ is the scattering angle and d_{hk} is the spacing between the parallel rows of atoms.

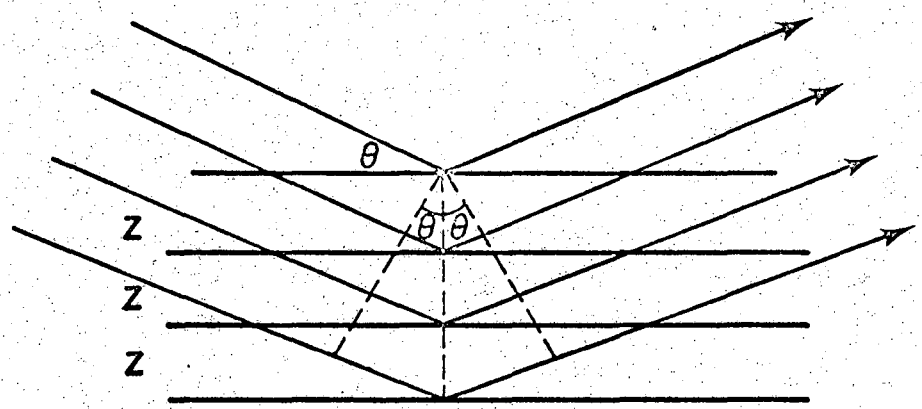

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Fig. 2c Constructive interference from planes which are z apart.

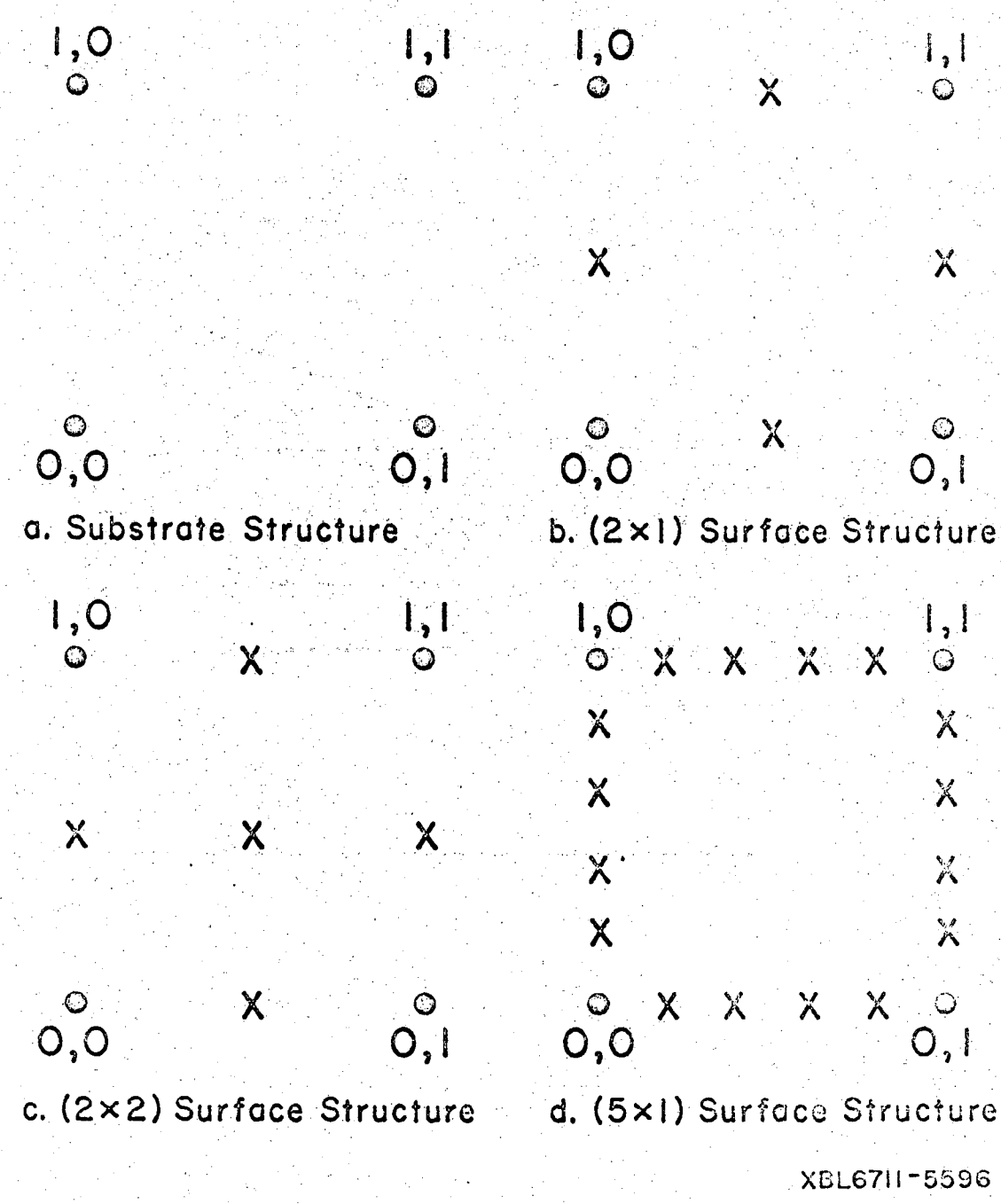

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Fig. 3 Diffraction patterns from a (100) face-centered cubic lattice.

⊙ Normal features X Extra features

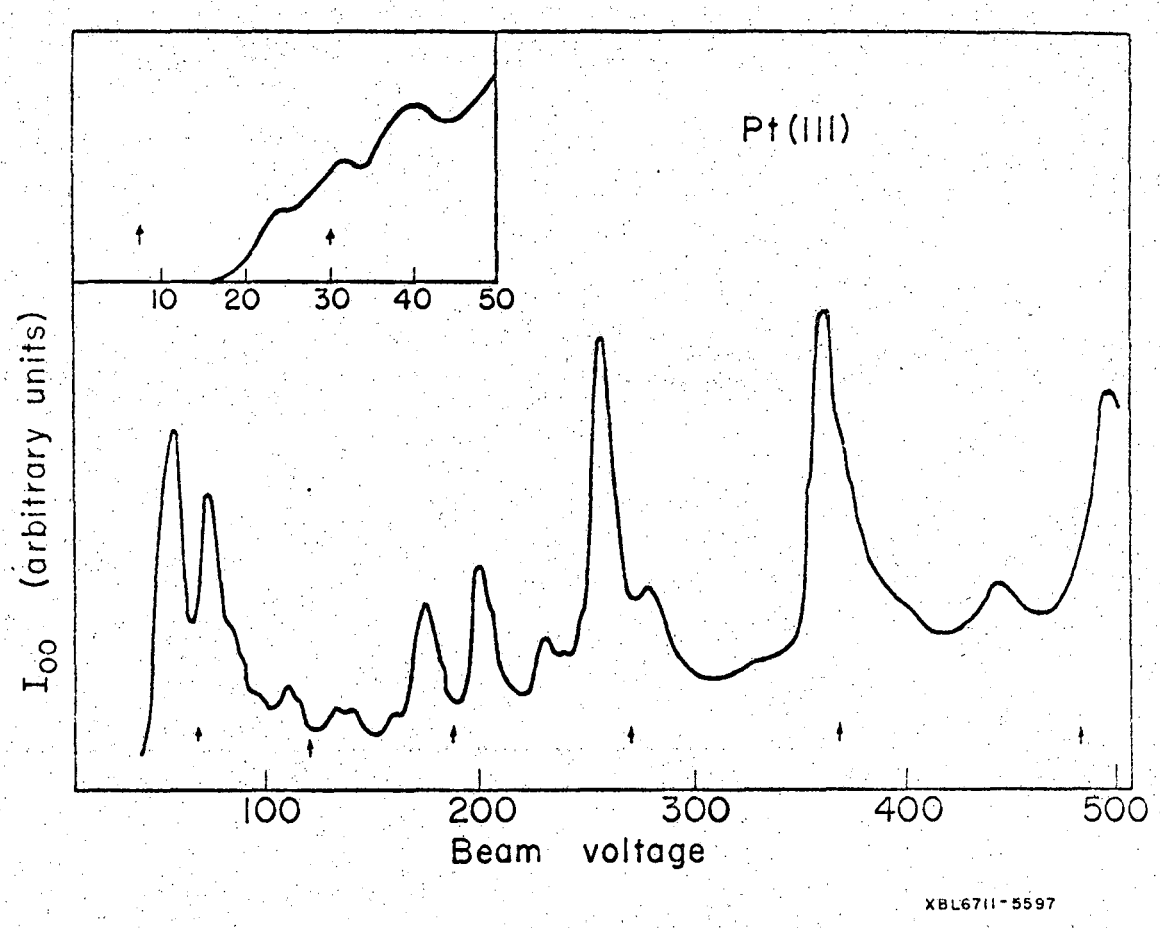

Fig. 4 Specular intensity (I_{00}) versus beam voltage (V) for Pt (111). Arrows indicate predicted Bragg maxima.

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