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Low-Energy Electron Diffraction

Improved experimental methods provide new information on the structure of surfaces of solids

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Interest in surface phenomena has increased markedly in the past few years. This can be attributed partly to the increased complexity and resultant unwieldy size of many electronic systems. The need for smaller components is pressing. This need can be obviated by making solid state components from thin films rather than from massive single crystals. Miniaturization of some systems is now feasible through the use of thin film resistors and capacitors.

Many problems in the construction of thin-film devices are related to the surface of the material used. Since the ratio of surface to volume for such devices is quite high, even the adsorption of gases on the surface can sometimes have a pronounced effect on the total characteristics of the device. Even the actual formation of the film is really a surface problem.

There are other areas of solid state technology that rely on surface phenomena. An example is the use of epitaxial layers in the manufacture of transistors. Probably the most important applications of surface phenomena to technology do not lie in the area of solid state physics, however. They may be applications from the field of catalysis and the related fields of oxidation and corrosion. The synthesis of numerous materials is often the result of reactions at the surfaces of catalysts.

While technology relies on surface reactions in these and other ways, the basic phenomena underlying these surface effects are not well understood. Much of our current understanding of surfaces is empirical. The knowledge of the bulk properties of matter is better understood. This is due, at least in part, to basic and detailed knowledge of the arrangements of atoms in solid crystals, knowledge which can be obtained by means of x-ray diffraction. The determination of crystal structures provided the impetus that was necessary for the mathematical treatment of solids. Preparation of very pure materials was another important development that aided in the understanding of the solid state, for only after such materials had been prepared could the intrinsic properties of solids be determined.

In the case of surfaces, the situation is quite different. In general we do not know the spatial arrangements of the individual surface atoms, nor has it been possible to prepare clean surfaces easily. Without knowledge of the spatial arrangements and with contaminated surfaces, in many instances advance in the science of surfaces has proceeded only by the method of trial and error. The recent improvement in low energy diffraction techniques promises to supply information that will contribute greatly to more exact understanding of surface phenomena.

Just as it is necessary to have ultrapure crystals to study their intrinsic properties, it is necessary to have surfaces free from adsorbed gases to study surface effects. Even if it were possible to produce a clean surface in air, serious contamination would occur in such a short time that it would be impossible to obtain measurements upon it. Thus it is necessary to work in a vacuum. The low pressures reached by ordinary vacuum systems are, however, not sufficient. At a pressure of 10^{-6} torr a surface becomes covered with a monolayer of gas in about 1 second. The use of recently developed ultrahigh vacuum techniques are a necessity for surface investigations. Pressures of the order of 10^{-10} torr can now be obtained quite easily with commercial equipment. In such a vacuum a clean surface obtained by cleaving, by ion bombardment, by chemical techniques, or by high-temperature heating will remain clean for a period of time that is usually sufficient to complete most necessary measurements. This article describes the determination of surface structures by means of low-energy electron diffraction, a technique that can be of value only if accompanied by vacuum techniques that permit a surface of controlled composition to be maintained.

For an understanding of surface phenomena the positions of the atoms that are at the surface of a crystal must be known. Even at a "clean" surface, the asymmetry of the forces on the surface atoms must result in an altered interatomic spacing. Attempts to measure such displacements by x-rays or by conventional electron diffraction, with 50 kev electrons, have not been successful. The ideal tool for such surface structure determinations is low-energy electron diffraction. This was recognized in the Davisson-Germer experiment of 1927. Structures resulting from gases adsorbed on a crystal were observed in this experiment that established the wave character of the electron (*1*), but the gas molecules on

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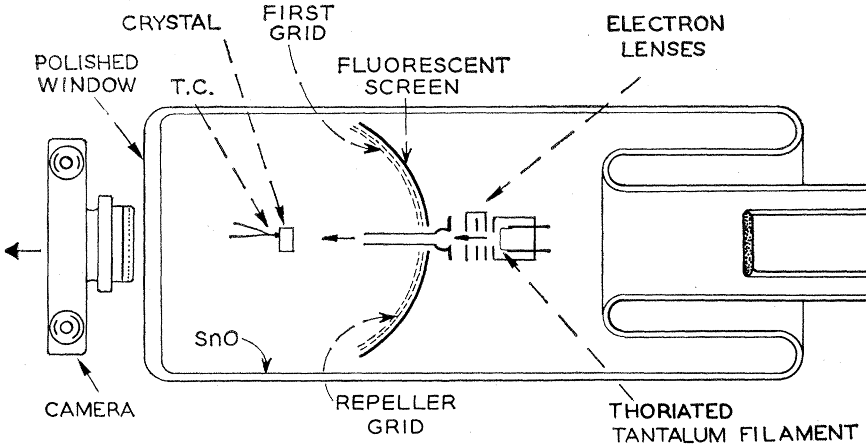


Fig. 1. Schematic drawing of the low-voltage electron diffraction tube. The electrons, originating from the filament at right, impinge on the crystal, pass through the two grids, and produce a diffraction pattern on the fluorescent screen. This pattern may be viewed or photographed through the window at left.

the surface (possibly carbon monoxide) were not identified in these early experiments. The low penetrating power of these low-voltage electrons, in contrast to the high penetrating power of x-rays, makes it possible to determine structures that represent a fraction of a monolayer of surface coverage.

In spite of the potential application of low-energy electron diffraction to surface structure determination, very little research has been done with this tool. After the first experiments, low-energy electron diffraction was quickly abandoned in favor of high- (50 kev) energy electron diffraction. This was mainly because of the experimental ease of handling fast electrons. These fast electrons have been used for some studies of surface phenomena, but they are much too penetrating for the investigation of adsorbed gases or catalytic reactions. H. E. Farnsworth has, however, recognized the usefulness of this tool and he and his students at Brown University have continued to use low-energy electron diffraction in their surface studies since the late 1920's.

The effectiveness of this research tool has been impeded by the laboriousness of the experimental procedure. The detection of the diffracted electrons with a Faraday box is a very time-consuming job. In addition, many of the detailed features of the diffraction pattern can be missed if the diffraction pattern is changing rapidly during the adsorption of gas. A more rapid technique was devised by W. Ehrenberg (*2*) in 1934 and has been recently perfected by a group at Bell Telephone Laboratories under the stimulation of L. H. Germer (*3*). Ehrenberg displayed diffraction patterns directly on a fluorescent screen by accelerating the diffracted electrons after they had passed through a fine cylindrically shaped metal grid placed between the crystal and the fluorescent screen. This grid served as a shield for the high voltage on the fluorescent screen. The diffracted electrons actually pass through two grids; the first is approximately at the potential of the crystal, and the second is at the potential necessary to reject all but the elastically scattered electrons, which are the only electrons that contribute to the diffraction pattern. Ehrenberg did not continue to develop this technique, and it was revived by the group at Bell Telephone Laboratories in 1959.

A schematic drawing of a recently improved post acceleration diffraction tube (*4*) containing spherical grids (*5*) is shown in Fig. 1. The low-energy electrons are focused at normal incidence on a small crystal by a series of electrostatic lenses and then diffracted in the backward direction. After passing through the two grids they are accelerated by a potential of 4 kilovolts to the fluorescent screen. It is possible to photograph or observe visually the diffraction pattern on the screen through the polished window at the front of the tube. The electrons have a wavelength $\lambda = 150/V)^{1/2}$, where λ is in angstroms. The apparatus is an integral part of a vacuum system that is capable of providing a pressure of 1×10^{-10} torr.

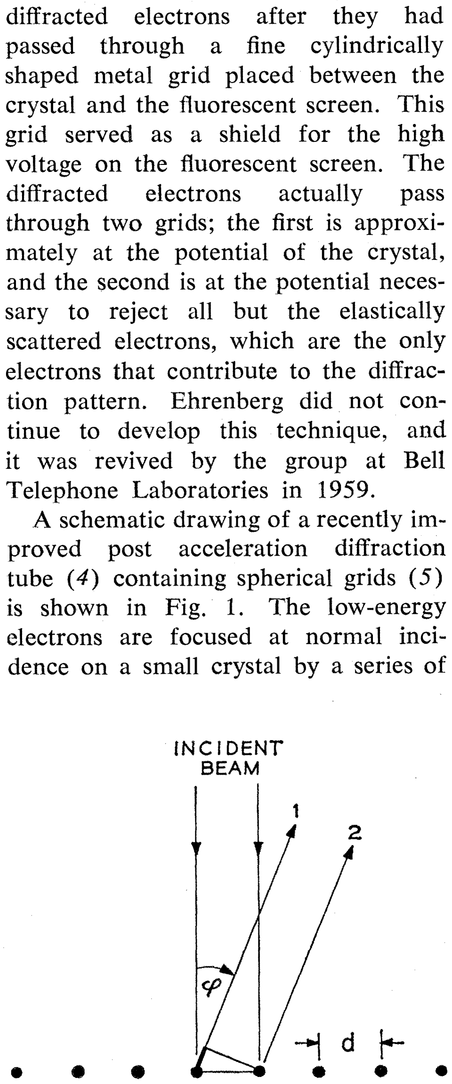


Fig. 2. Diagram illustrating the origin of the grating formula. The dots represent rows of atoms on the surface. The dark side of the triangle represents the path-length difference $d \sin \phi$ between beams 1 and 2.

Many experiments that were previously extremely tedious or impossible can be performed with this equipment. For example, continuous adsorption of gas on a surface often causes the diffraction pattern to change rapidly. The rapidly changing patterns can be observed visually and convenient permanent records of the diffraction patterns can be obtained by photography. It is even possible to determine the variation in the intensity of a particular spot with a photometer equipped with a photomultiplier tube and appropriate optics. By focusing such a device on one diffraction spot, in just a few minutes the dependence of the intensity of this spot on the wavelength of the incident electrons can be obtained through a wide range of voltage. The diffraction tube is normally operated with electrons whose energies are from 6 to 600 volts (5 to 0.5Å), but the most useful range is usually between 50 and 150 volts. A complete diffraction pattern throughout an arc of 180° can be displayed on the screen by operating the first grid at a positive voltage with respect to the crystal. Electrons normally diffracted outside the solid angle subtended by the screen are then attracted to the grid system. Although distortion of the pattern does occur, it usually does not introduce complications into the analysis of the patterns.

With this recently perfected tool it should now be possible to obtain new information on the structure of surfaces which may simplify the interpretation of many previously established surface effects and result in the discovery of new surface phenomena. This, in conjunction with auxiliary surface studies of field emission, photoelectric emission, surface transport properties, infrared spectroscopy, and chemical kinetics, may make our understanding of surfaces comparable to the present understanding of the bulk properties of crystals.

This article is a summary of some of the surface studies of single crystals of nickel performed with the low-energy electron diffraction technique. This is intended, by way of illustration, to draw attention to the wide potential uses of this method.

Two Dimensional Crystallography

Since low-voltage electrons are scattered predominantly by the first layer of atoms of a crystal, the diffraction patterns have many characteristics of a two-dimensional diffraction effect. Actually we are all more familiar in everyday life with two-dimensional diffraction effects than we are with either the one- or three-dimensional types. For example, the cross of light that is observed when one looks at a distant street light through the screen on a porch is the result of the two-dimensional grating formed by the screen.

The atoms on a surface form rows with uniform spacings. These rows are analogous to the lines of a diffraction grating; in fact, the location of the diffraction spots in the low-voltage diffraction pattern can be interpreted as arising from crossed diffraction gratings. A diffraction spot occurs at those angles ϕ in Fig. 2 for which the path difference between the scattered beams marked 1 and 2 is an integral number of wavelength—that is, whenever the path difference $d \sin \phi$ equals $n\lambda$, where n is an integer and d is the spacing between similar rows of atoms. As the wavelength is decreased—that is, as the voltage is increased—a given diffraction spot will move toward the center of the screen.

A marble model of a cube or (100) surface of a clean nickel crystal is shown in Fig. 3*a*. A photograph of the low-energy electron diffraction pattern from a similarly oriented crystal is shown in Fig. 3*b*. The surface atoms in this model are at the corners of squares, and the diffraction pattern confirms this symmetry. It is convenient to identify the diffraction spots by two-dimensional Miller indices. A suitable unit mesh is first chosen; in the case of the (100) surface it is the square. Thus the diffraction spots are indexed 00,10, . . . , *hk* as indicated in Fig. 3*b*. The 00 spot is the spot produced by the specular reflection of the incident beam.

Comparison with X-ray Diffraction

For readers who are familiar with the use of x-rays for the determination of structure it is informative to compare low-energy electron diffraction to x-ray diffraction. In some respects back-reflection x-ray diffraction is similar to the technique discussed here. In both cases the diffraction pattern is observed in the backward direction. Although the array of spots obtained with both these techniques may have a similar appearance, they cannot be similarly interpreted. One big difference is that white radiation (radiation having a distribution of wavelengths) is used in the x-ray case whereas monochromatic—that is, one wavelength, or monoenergetic—electrons are used in electron diffraction.

The interaction of x-rays and electrons with the crystal is illustrated by examining the reciprocal lattice used with these two techniques. The concept of a reciprocal lattice provides a convenient geometrical basis for the analysis of diffraction patterns. It represents an easy visualization of the orientation of the crystal and the important spacings between atomic rows or planes in the crystal. A cross-sectional view of the reciprocal lattice of a face-centered cubic crystal is drawn in Fig. 4*a*. The *hkk* points are in the plane of the paper and the incident beam strikes the (100) face. Each one of these points represents a reflecting plane in the crystal and the distance from the origin is just the reciprocal of the crystal-plane spacing.

If a sphere with a radius equal to the reciprocal of the wavelength is drawn with its circumference touching the origin, a reflection will occur whenever one of the reciprocal lattice points is intersected. For the particular value of λ in Fig 4*a*, only the 311 reflection is obtained. A reflection will occur whenever $(2/\lambda) \sin \theta = 1/d_{hkk}$ where d_{hkk} is the spacing between the *hkk* planes. This is just the Bragg equation. If an arbitrary value of the wavelength had been used, it would be highly fortuitous for a reflection to occur at all. Thus in the case of back-reflection x-ray diffraction with a stationary crystal, radiation containing many wavelengths is used. Numerous reciprocal lattice points are then intersected by a continuous family of reflection spheres and produce the diffraction pattern characteristic of this technique.

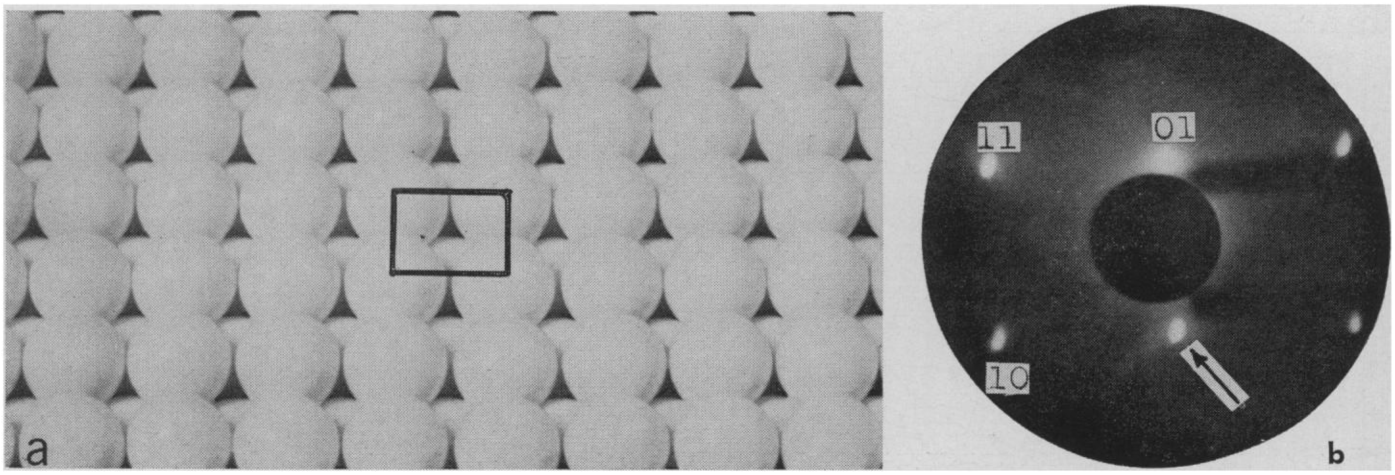


Fig. 3. (*a*) A marble model of the (100) surface of a face-centered cubic crystal. The unit mesh is outlined. (*b*) Low-energy electron diffraction pattern from a clean Ni(100) surface, with 132-volt electrons. The crystal is rotated slightly with respect to the incident beam to display the 00 spot, marked by the arrow. The two-dimensional Miller indices of the spots are indicated. A shield behind the crystal obscures the center of the screen.

The use of such a reciprocal lattice is valid only if coherence is obtained from many three-dimensionally arranged scattering centers. This does not take place for low-energy electron diffraction. The scattering occurs predominantly from the topmost layer of atoms and in many respects it is two-dimensional in nature. The reciprocal lattice of a face-centered cubic crystal for incident low voltage electrons, shown in Fig. 4*b*, consists of rods rather than points. The important distance now is d_{10}, the largest distance between adjacent rows of atoms. We see that the sphere of reflection now intersects at least one rod and produces a diffraction spot even when monochromatic radiation is used. The 00 diffraction spot always occurs at low voltage because the sphere of reflection intersects the 00 rod for any value of λ. The 10 rod is intersected for all values of $\lambda < d_{10}$. The plane grating formula $(1/\lambda) \sin \phi = 1/d_{10}$ is determined from this figure by considering the outlined triangle.

Low-voltage electron diffraction is, of course, not strictly a two-dimensional phenomena. The incident electrons do penetrate slightly into the crystal and coherence between the scattering from the atoms on the surface and from those in the second or third layer has to be considered. A modulation in the intensity of diffraction spots, including the 00 spot, is thus observed when the voltage is changed.

This situation can be represented by a reciprocal lattice of rods of variable density which may be heaviest at or near the positions of the reciprocal lattice points. The density of the rod is then a measure of the intensity of a spot. A particular diffraction beam is then observed over a continuous range of wavelengths and the intensity maxima occur whenever the sphere of reflection intersects reciprocal lattice rods at their densest points. The intensity does not necessarily go to zero at points of intersection of the rods midway between the reciprocal lattice points. This is the result of the strong scattering produced by the topmost layer of atoms. The amplitude distribution along the rods can be quite complicated. This topic is illustrated later with some results on nickel. From an analysis of the diffraction pattern and the voltage dependence of the intensities it is thus possible to determine both the two- and the three-dimensional aspects of surface structures.

It is necessary to determine the arrangement of atoms at the surface of a metal before the interaction of gases with the clean surface can be understood. The diffraction pattern of the (100) surface of nickel shown in Fig. 3*b* indicates that the nickel atoms in the topmost layer of this surface have exactly the same arrangement as the atoms in similar planes in the bulk of the crystal. This is also true for the nickel atoms on both the (111) and (110) planes. Diffraction patterns of these surfaces are shown in Figs. 5 and 6 together with the marble models of these surfaces. In all these cases these diffraction patterns indicate the positions of the atoms in the surface planes. While these surfaces of nickel have the same atomic arrangement in the surface as in the bulk of the crystal, it is not true that all crystals exhibit this simplicity. Elemental silicon and germanium, both semiconductors, in fact have surface structures that are quite unlike those of the bulk structures (*6*). Their surface structures are the result of complete reconstruction of the positions of the surface atoms and are responsible for interesting chemical effects (*7*).

Since electrons penetrate a crystal a finite distance, it should be possible to

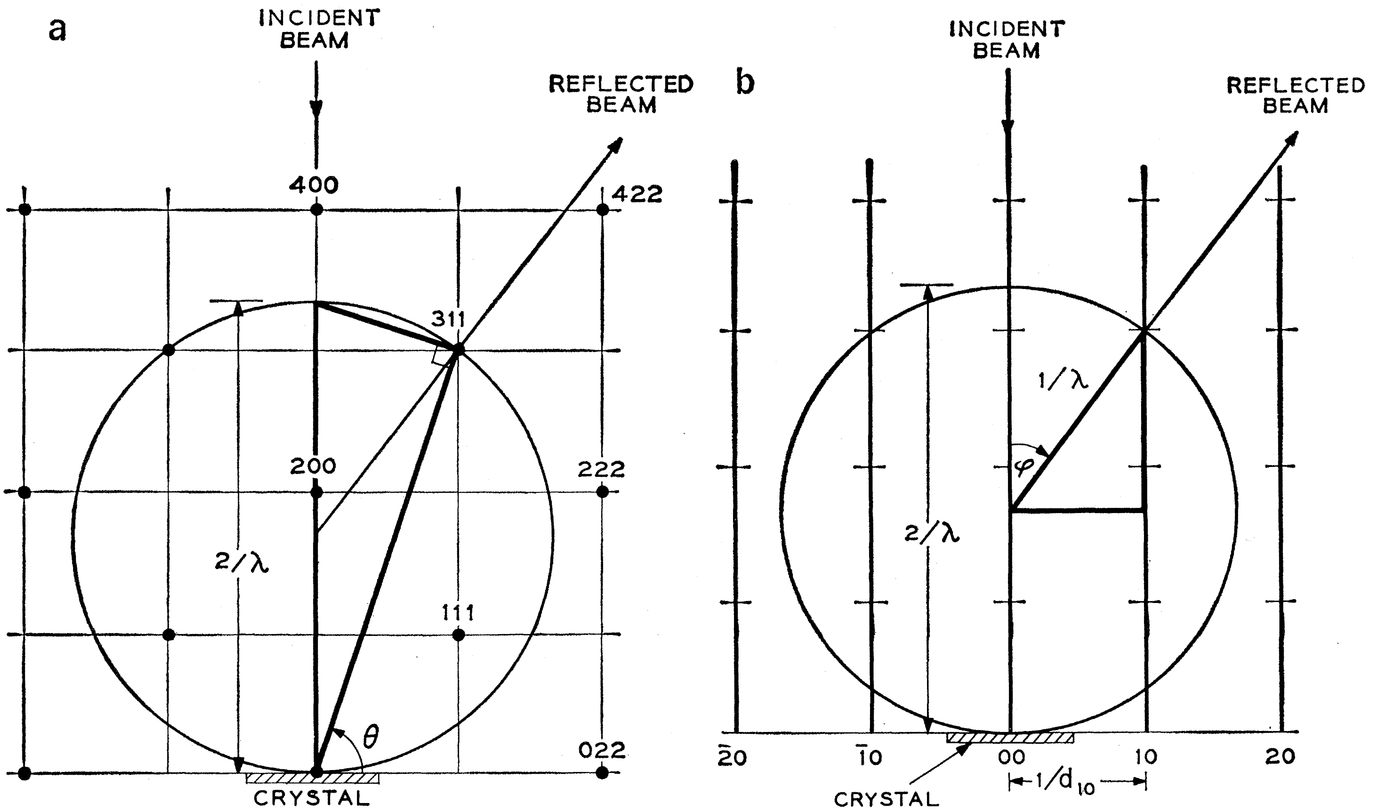


Fig. 4. (*a*) Part of the reciprocal lattice of a face-centered cubic crystal for penetrating radiation. The beam is incident on the (100) surface. The Bragg equation $n\lambda = 2d_{hkl} \sin \Theta$ can be established from the outlined triangle. (*b*) Reciprocal lattice of a face-centered cubic crystal for weakly penetrating radiation. The discrete points of Fig. 4*a* are replaced by rods.

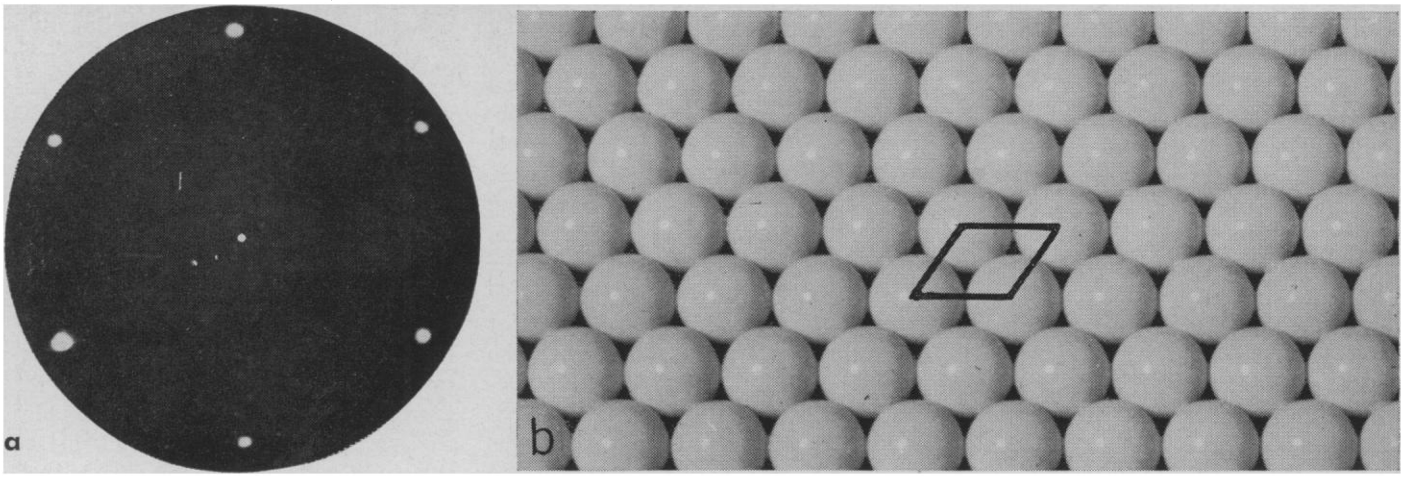


Fig. 5. (*a*) Diffraction pattern from a clean Ni(111) surface, with 94-volt electrons. The 00 spot is at the center of the screen. (*b*) Model of the (111) surface of a face-centered cubic crystal. The unit mesh is outlined.

determine the spacing between the topmost surface layer and the second layer and to make a comparison with a similar spacing in the bulk of the crystal. This can be done by measuring the dependence of the intensity of particular diffraction spots on the wavelength of the incident electrons. In general, the relationship between intensity and wavelength exhibits many maxima and minima, and interpretation has turned out to be quite complex.

The most intense maxima usually occur whenever the sphere of reflection in Fig. 4*b* passes through or close to a reciprocal lattice point. To obtain agreement between the calculated and experimentally determined positions of these maxima it is necessary to make allowances for the energy increase of the electrons as they enter the crystal from the vacuum. This is referred to as the inner potential of the crystal and is about 16 volts for nickel.

It is extremely difficult to prepare a crystal with an absolutely planar surface. The surface will contain steps and intensity maxima will occur as a result of the coherence between the scattering from atoms at the top and bottom of these steps. Since these electrons do not penetrate the crystal the resulting maxima will not be displaced by the inner potential. The dependence of the intensity of one particular diffraction spot from a clean (111) surface of nickel on the voltage of the incident electron is shown in Fig. 7. The most intense maxima, marked by the long arrows, are due to coherence between the scattering from atoms in the bulk of the crystal. These arrows have been shifted from their calculated positions to lower voltage by 16 volts to take into account the inner potential of the nickel crystal. The short arrows to the right indicate the calculated position of the maxima due to steps on the surface. The short inverted arrows to the left of the long arrows mark still a third type of maximum that is the result of a 5 percent expansion of the distance between the topmost and the second plane of atoms. Similar peaks have been observed in the other diffraction spots from this (111) surface of nickel and are consistent with this increased separation. An increase in the spacing between the surface atoms and atoms of the second plane of about the same amount has been observed also for other planes of nickel (*8*).

The intensity of a diffraction beam obtained from a crystal is not determined only by the mean positions of the diffracting atoms, as one might perhaps surmise from this discussion. If the scattering from all of the atoms in a crystal is exactly in coherence, the diffraction beams will have their maximum intensity. A displacement in the position of these atoms will result in a

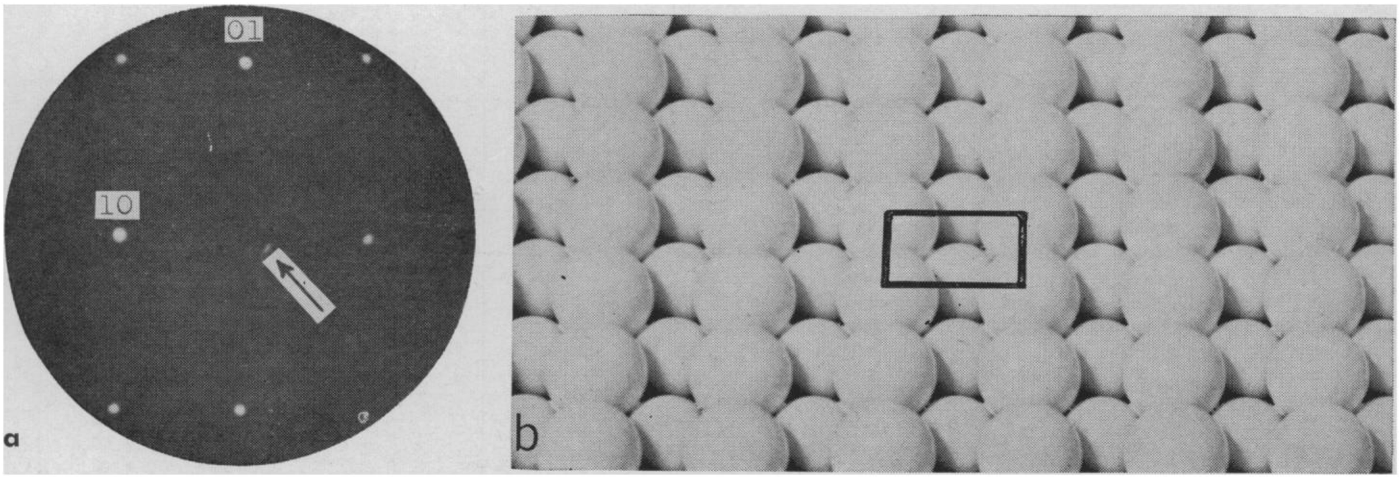


Fig. 6. (*a*) Diffraction pattern from a clean Ni(110) surface, with 80-volt electrons. The arrow indicates the position of the 00 spot. (*b*) Model of the (110) surface of a face-centered cubic crystal. The unit mesh is outlined. This surface is characterized by troughs in the [110] direction on the surface.

decrease in the intensity. Such a displacement occurs as the atoms undergo thermal vibration. This is well known in the case of x-rays where it is referred to as the Debye-Waller effect. The amplitude of the thermal vibrations is modified at crystal surfaces, and this modification can be detected by low-energy electron diffraction techniques. Atoms in the bulk of a nickel crystal must vibrate under the restraining forces of their 12 nearest neighbors. Surface atoms have fewer neighbors and are consequently subject to lower restraining forces. This results in a greater thermal vibrational amplitude. When some of the atoms are displaced from their mean positions because of thermal vibrations, the intensity of a diffraction spot is decreased. Since the frequency of the incident electrons is much greater than the vibrational frequency of the atoms, the electrons essentially sample the instantaneous position of the atoms. Thus, as the temperature of the crystal is increased the intensity of diffraction spots is decreased because of the increased vibrational amplitude.

The dependence on temperature of the intensity of a diffraction spot from the (111) face of nickel at 135 volts is shown in Fig. 8. The dashed line represents the temperature dependence that would be observed if the scattering originated in the bulk of the crystal. Indeed, such a dependence is observed in the case of electrons when the penetration into the crystal is appreciable at high voltages. At lower voltages, when the contribution to the scattering from the surface atoms is considerable, we observe a marked increase in the absolute value of the slope of this curve because the vibrational amplitudes of the surface atoms are greater than the amplitudes of the bulk atoms (*9*). Before it is possible to determine the vibrational amplitude of surface atoms from such curves, it is necessary to assess the relative scattering contributions of both surface and bulk atoms. This work has not been completed.

Interaction of Gases with Surfaces

The above studies of clean crystal surfaces pave the way for the investigation of the adsorption of foreign atoms and molecules on a clean surface, their reactions with the surface, and with each other. Reactions of this type form the basis of corrosion, oxidation, and catalysis. Without a thorough understanding of the clean surface it is difficult to interpret such experiments.

The number of structures that can be formed by the interaction of one gas with a particular crystal can be quite large. This is partly because the symmetry of the surface structures formed by the foreign atoms is usually similar to the symmetry of the surface of the substrate crystal. Just as it is possible to vary the relative composition of a mixture of two elements and observe different three-dimensional crystalline structures, it is possible also to vary the amount of gas adsorbed on a particular surface and to observe different surface structures. The phase diagrams of two-dimensional interactions are actually more complicated than those of three-dimensional interactions because of the larger number of variables present.

The three closest packed surfaces of nickel, the (111), the (100), and the (110) represent an interesting system of increasing complexity. Atoms on these surfaces have, respectively, 9, 8, and 7 nearest neighbors rather than the usual 12. Because of this, one would expect to observe separate and different chemical effects on these surfaces. This is just what occurs. Surface structures exhibiting the symmetry of the substrate

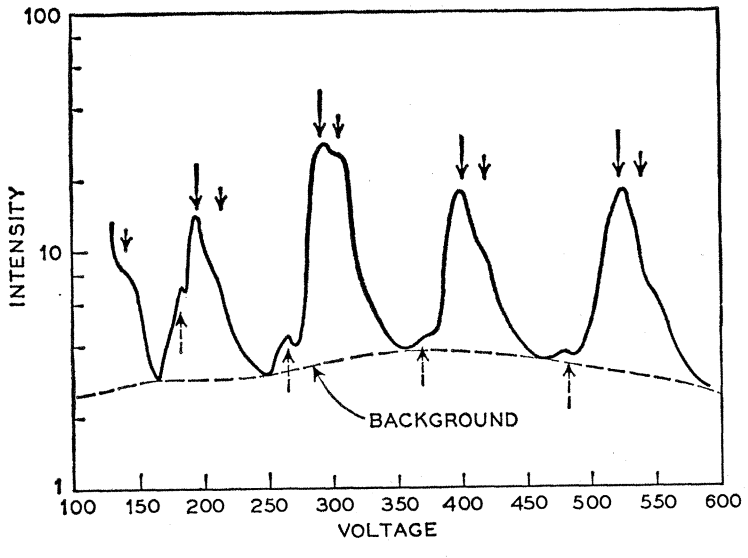


Fig. 7 (above). Dependence of the intensity of the 01 spot from a Ni(111) surface on the voltage of the incident electrons. The long arrows mark the calculated positions of the maxima with an inner potential of 16 volts. The short arrows are the positions of maxima determined by steps on the surface, and the inverted dashed arrows are the calculated positions of maxima due to a 5-percent normal expansion of the top surface layer.

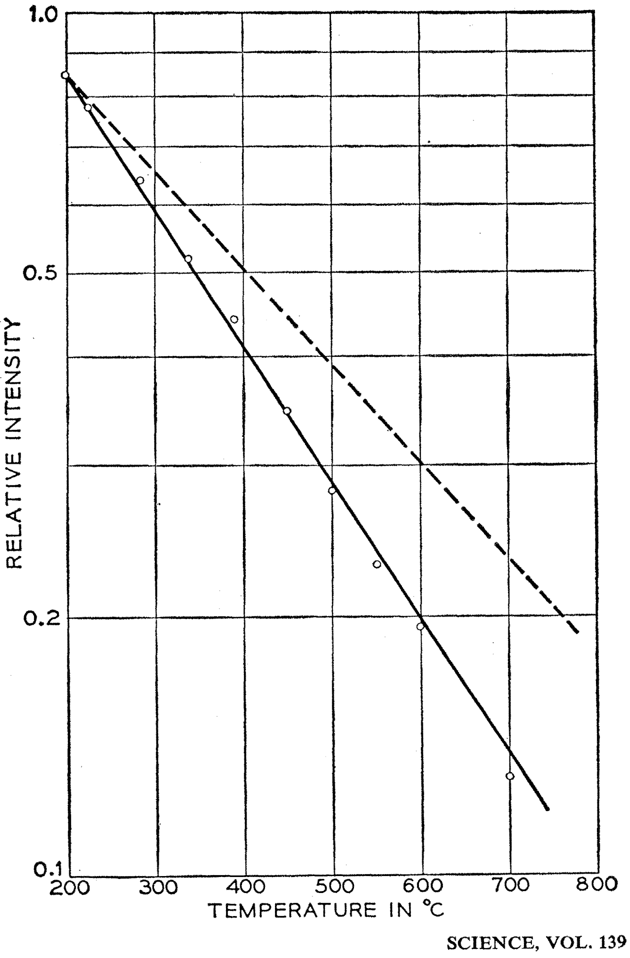


Fig. 8 (right). Temperature dependence of the intensity of the 00 spot from a clean Ni(111) surface, with 135-volt electrons. The dashed curve represents the dependence expected for highly penetrating radiation.

crystal are observed to form when oxygen is adsorbed on both the (111) and (100) surfaces, but since the (110) surface, which is relatively open, exhibits interesting phenomena of considerable complexity, much of the following discussion is related to this surface.

The (110) surface is characterized by troughs formed by the surface atoms. These troughs, shown in the marble model of Fig. 6*b*, apparently play an important role in adsorption processes on this surface. While some structures observed during the adsorption of gases on the more dense faces are composed of gas atoms only, structures observed on the (110) face are in general the result of a reconstruction of the surface and involve the surface migration of nickel atoms (*10*). Effects of this type have also been observed for silicon and germanium (*7*).

Adsorption of Oxygen on a (110) Surface of Nickel

The adsorption of gases accompanied by a reconstruction of the substrate structure is an interesting and often overlooked process of chemisorption. The adsorption of oxygen on the (110) surface of nickel is an example of such a process and illustrates the usefulness of low-voltage electron diffraction in gas adsorption studies (*11*).

A diffraction pattern that is observed from this surface soon after baking the vacuum system at 400°C but before the crystal has been completely cleaned is shown in Fig. 9*a* (*12*). This pattern contains diffraction spots of fractional order, not present in Fig. 6*a*, and it is produced therefore by a surface that is not clean. The structure deduced from the pattern of Fig. 9*a* is shown in Fig. 9*b* and is designated as a $c(2\times2)$ structure. The "(2×2)" symbol indicates that the unit mesh of this structure has dimensions twice that of the unit mesh of the clean nickel (110) substrate in both the [10] and [01] surface directions and the "*c*" means that this structure is centered. The impurity responsible for this structure is probably carbon. Apparently the carbon results from the decomposition of hydrocarbons that were adsorbed on the surface of the crystal before it was mounted in the vacuum system. The gray marbles in Fig. 9*b* represent nickel atoms that have migrated along the surface in the presence of the carbon to form this structure. The carbon atoms, not shown in this figure, presumably are located in the spaces between the surface nickel atoms. Although we see no diffraction features due to them, we know that they

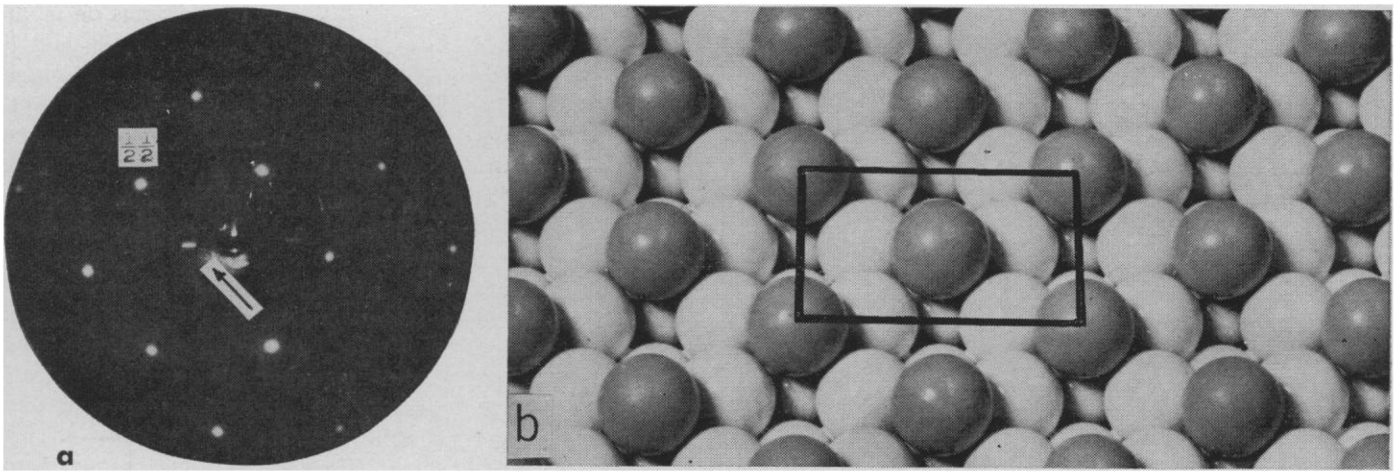


Fig. 9. (*a*) Diffraction pattern from a $c(2 \times 2)$ structure on a Ni(110) surface, with 80-volt electrons. The position of the 00 spot is marked by the arrow. The $h/2$ $k/2$ spots are due to the presence of carbon on the surface. (*b*) The $c(2 \times 2)$ structure on the (110) surface. The gray marbles represent surface nickel atoms. The carbon atoms are not shown, but they are probably located in the holes between the surface nickel atoms. The new unit mesh of this structure is outlined.

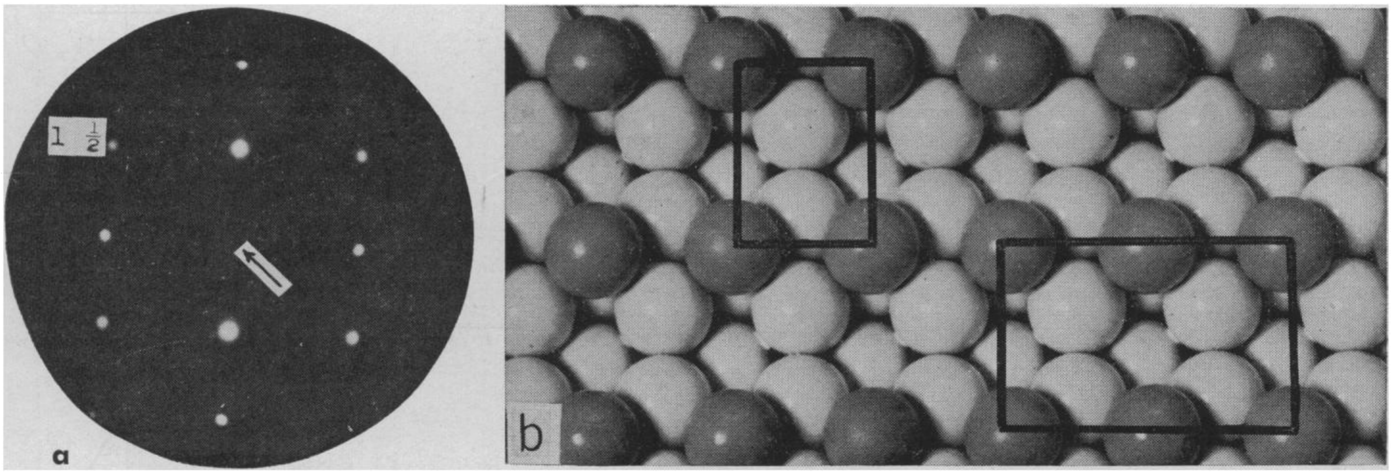


Fig. 10. (*a*) Diffraction pattern from a (1×2) structure on a Ni(110) surface. The arrow denotes the position of the 00 spot. The spots due to the (1×2) structure have fractional indices. (*b*) The (1×2) structure on the 110 surface produced by the adsorption of oxygen. The gray marbles represent surface nickel atoms. The oxygen atoms are located between them in the troughs. This mesh is outlined in the center of the model. The mesh due to the pseudo NiO is shown at the lower right.

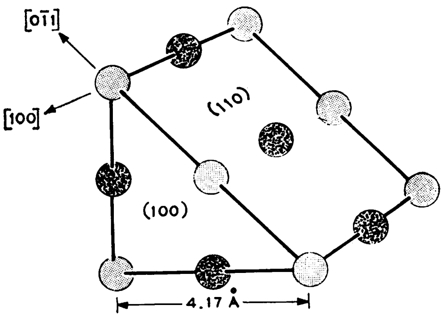


Fig. 11. A drawing of the NiO structure with a cut made along the (110) surface. Dark balls, oxygen atoms; light balls, nickel atoms.

too must be arranged in a similar $c(2 \times 2)$ structure.

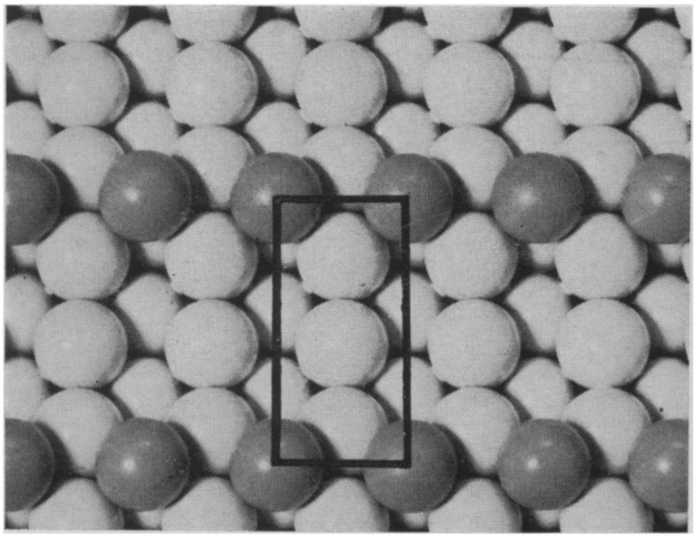
It is not possible to remove the carbon by heating alone. Apparently this nickel-carbon bond is so strong that the carbon is not vaporized, even at a temperature slightly below the melting point of the crystal, 1450°C. While bombarding the surface with argon ions may possibly remove the carbon, chemical removal can be effective. The carbon is easily oxidized and removed as carbon monoxide when the crystal is heated to 200°C in oxygen at a pressure of 1×10^{-7} torr. Under these conditions oxygen and the substrate nickel interact to form a tightly bound (1×2) structure which is discussed in another paragraph. The cleaning procedure is completed when the oxygen itself is removed by heating in hydrogen. Although hydrogen too is bound to the surface, it is removed by a moderate heating to 100°C (*13*). A surface prepared in this manner, or by ion bombardment, produces the diffraction pattern of Fig. 6*a* which contains only integral order diffraction spots. It is on this clean (110) face of nickel that oxygen adsorption studies have been made.

When oxygen is introduced into the vacuum system at a pressure of 5×10^{-9} torr the first change in the diffraction pattern is the development of streaks connecting the 00 and 01 spots, the 10 and 11 spots, and so forth. These streaks rapidly coalesce into spots and yield the diffraction pattern of Fig. 10*a*. Just from a visual inspection of this pattern one sees that a new structure has formed on the surface with a unit mesh whose dimension in the [01] direction is twice that of the substrate and equal to that of the substrate in the [10] direction. Such a (1×2) structure is shown in Fig. 10*b*. As in the case of the $c(2 \times 2)$ structure, the new fractional order spots have a high intensity which must be attributed to nickel atoms. The adsorption of oxygen on this face is thus accompanied by the migration of nickel atoms on the surface to form this structure. What is quite remarkable is that this occurs even at room temperature. The streaks that are observed initially are due to structural disorder in directions parallel to the troughs. The coalescing of these streaks into spots seems to indicate that the nickel atoms are migrating along the troughs that are so prominent in the marble model of Fig. 6*b*.

Only the nickel atoms in the (1×2) structure are shown in the model of Fig. 10*b*. The oxygen atoms are presumed to be located in the holes between the nickel atoms represented by the gray marbles. In many respects this structure is similar to the arrangement of nickel and oxygen atoms on the (110) face of nickel oxide (NiO). As shown in the drawing of NiO in Fig. 11, rows of Ni and O alternate in the [100] direction. This is just the arrangement of these atoms in the (1×2) structure, except for a scale factor. The arrangement is outlined in black in the (1×2) structure of Fig. 10*b*.

The (1×2) structure can be thought of as a (110) plane of a pseudo form of NiO in which the spacings are greater than the real oxide by 19 percent. The oxygen that is initially adsorbed on a (110) surface of nickel forms this chemisorbed structure that is similar to NiO.

The (1×2) structure is altered by the adsorption of additional oxygen. Keeping the pressure at 5×10^{-9} torr causes the fractional order spots in this structure to streak parallel to the troughs and gradually to form new spots that are indicative of a transition type structure. This new structure is a combination of (1×2) and (1×3) structures and is composed also of both nickel and oxygen atoms in the top surface plane. With additional oxygen exposure these spots also become streaked and then are resolved into sharp fractional order spots at the $h\ k \pm 1/3$ positions. Thus the structure responsible for these spots is appropriately called the (1×3) structure.



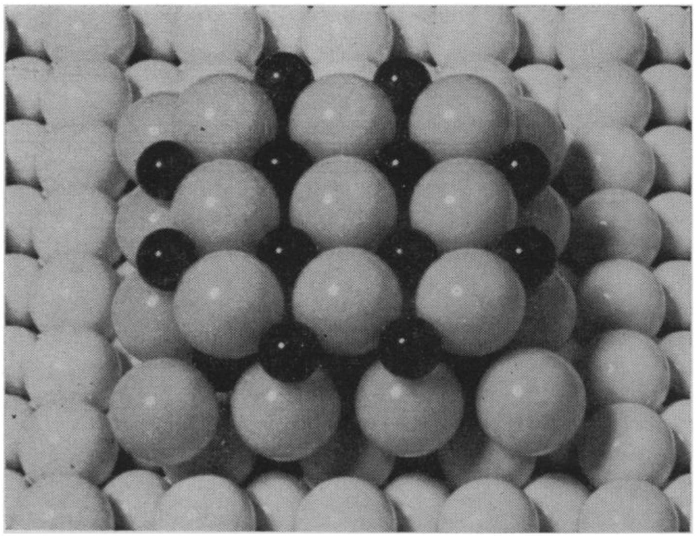


Fig. 12 (left). The (1×3) structure on the (119) surface. The new surface mesh is outlined. Fig. 13 (right). Model of (100) oriented NiO on the (110) surface of nickel. The epitaxially grown crystal does not have the same orientation as the substrate. These models are to scale. The small balls in the NiO model represent nickel ions; the large balls, oxygen ions.

A model of it is shown in Fig. 12. In going from the (1×2) structure, to the transition structure, to this (1×3) structure, the surface oxygen coverage has increased in discrete steps from 50 to 60 percent and then from 60 to 67 percent of a monolayer. The (1×3) structure forms at a much lower rate than the (1×2) structure. While every oxygen molecule that strikes the clean surface dissociates and is incorporated into the (1×2) structure only one in every ten incident molecules is incorporated into the (1×3) structure.

In some instances the adsorption of additional oxygen causes another structure to form. This is a (1×5) structure and represents 80 percent oxygen coverage. In most instances, however, the additional oxygen causes the intensity of both the integral and fractional order spots to decrease and eventually no diffraction pattern can be seen on the fluorescent screen. The strong background resulting from elastic scattering indicates that the surface is covered with an amorphous layer of oxygen. This must, in the limit, be several layers thick since the incident electron beam is not able to penetrate it to form a diffraction pattern from the underlying nickel.

In these transition patterns the presence of streaks parallel to the 0*k* zone, indicates that the nickel atoms forming these structures migrate along the troughs. Apparently these troughs provide a direction of easy movement for the nickel atom in the presence of oxygen, even at room temperature. This low temperature should be compared with 300°C (~ 600°K), the estimated temperature for the onset of surface migration on clean nickel. This later figure was estimated from the empirical rule that surface migration starts to take place at a temperature that is about one-third the absolute melting point of a metal (*14*).

Most of this adsorbed oxygen can be removed by heating the crystal. The amorphous layer of oxygen is removed at the fairly low temperature of 150°C, and the previously formed structures are removed at progressively higher temperatures. Each of these structures is a stable entity below its evaporation temperature because each structure has its own characteristic binding energy in relation to the nickel substrate. The (1×2) structure is the final one obtained by heating the crystal and appears to be stable up to the melting point of nickel (1450°C).

Epitaxial Nickel Oxide

None of the structures described in the previous section represent the true oxide. All of them have dimensions that are integral multiples of the underlying (110) unit mesh of the nickel and not the dimensions of NiO. It is, however, possible to form NiO on this face. At a relatively high temperature, 500°C, and a relatively high oxygen pressure, 10^{-6} torr, the oxide does form on the surface. The nickel oxide grown under these conditions does not assume the (110) orientation of the substrate nickel surface, however. It is the cube or (100) face that forms in the plane of the surface. This is shown in Fig. 13. From the features of the diffraction spots characteristic of the NiO, it is possible to determine how the oxide grows. The oxide does not cover the surface uniformly during the initial stage of growth. Small patches nucleate on the surface at what seem to be random positions but which may be determined by surface imperfections. The diffraction spots produced by these patches are weak and diffuse; they gradually become more intense and definitive as the individual patches grow larger in size and finally cover the entire surface. At this point it is no longer possible to see the diffraction spots characteristic of the nickel substrate.

The oriented growth of NiO occurs also on both the (100) and (111) surfaces of nickel. The most stable oxide on these surfaces, in contrast to the oxide formed on the (110) surface of nickel, has the same orientation as the substrate nickel crystal. These NiO diffraction spots initially are weak and diffuse because of the small size of the patches. As the patches get larger and eventually cover the entire surface the spots become sharper. A typical diffraction pattern obtained from the oxide on the (111) face of nickel is shown in Fig. 14. The superposition of the diffraction patterns obtained from the (111) face of NiO and that obtained from the (111) face of Ni indicates that only part of the surface is covered with the oxide. The diffraction spots of the NiO are closer to the center of the screen than the spots from Ni since the lattice constant of the oxide is 18 percent larger.

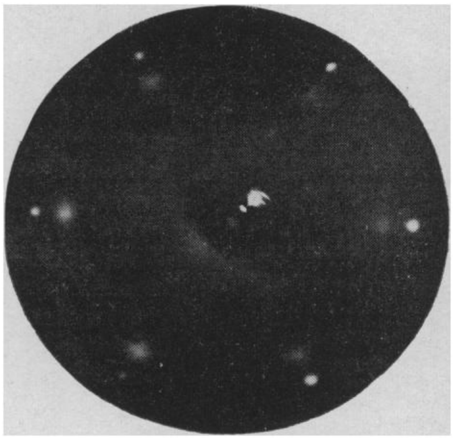


Fig. 14. Diffraction pattern from a (111) oriented epitaxial layer of NiO on a Ni(111) surface, with 90-volt electrons. The six outside spots are from the nickel; the diffuse, less intense spots are from the NiO(111).

The diffraction patterns resulting from the oxide oriented on the (111) surface reveal information that is not contained in the patterns from either the oxide-covered (100) or (110) surfaces (*15*). At low voltages, between 15 and 25 volts, three extra spots appear in the diffraction pattern. These behave in a peculiar manner as the voltage is increased; instead of moving towards the center of the screen, they move outward and eventually go off the screen. The presence of inclined planes on the surface accounts for this apparently anomalous motion. As shown in Fig. 15, a plane inclined to the surface of the crystal will have its own diffraction pattern, which will appear partially on the fluorescent screen. A first order diffraction beam, making an angle ϕ with the incident beam, will move toward the new specularly reflected or 00 beam as the voltage is increased. This movement appears on the diffraction pattern as an increase in the angle ϕ, and accounts for the unusual motion of these spots.

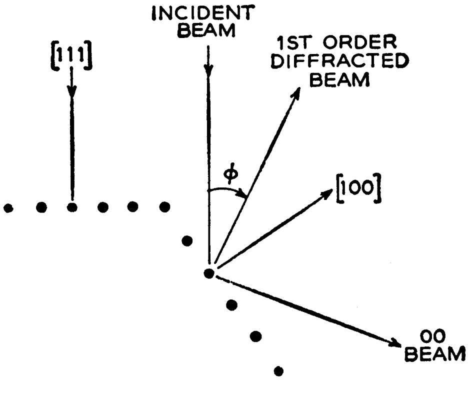


Fig. 15. A second diffraction pattern is produced by reflections from an inclined plane.

Since the three spots are not present

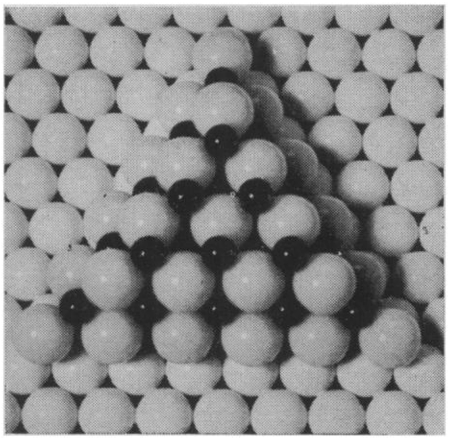


Fig. 16. Model of (111) oriented NiO on the (111) surface of nickel. This NiO forms pyramids having (100) faces. New diffraction patterns are produced by reflections from these inclined faces.

in the patterns obtained from the clean surface, it is evident that the (111) oriented NiO grows in the form of three-sided pyramids. Such a structure could presumably have sides with either (110) or (100) oriented faces. Comparing the experimental results with the calculations of the angular dependence of these spots on voltage reveals that it is the (100) plane that forms the faces of these pyramids, not (111) planes. Thus, the NiO that grows on this (111) surface of nickel is constrained to grow with the same orientation as the nickel; however, once it starts to grow, the most stable plane of oxide forms the faces of the structure as shown in Fig. 16. The three extra spots that are observed at low voltages are produced by the faces of this triangular-shaped pyramid.

These results indicate that the (100) plane is the most stable plane of nickel oxide. That this is so can be seen by counting the number of missing nearest neighbors on its principal planes. Each anion, as well as each cation in the bulk of the crystal, has six nearest neighbors. At the surface of the crystal the number of such missing neighbors per unit area is $4/a_0^2$ for the (100) face, $4\sqrt{2}/d_0^2$ for the (110) face and $4\sqrt{3}/a_0^2$ for the (111) face. Apparently the initial crystallites that form on the surface of the nickel grow in such a way that the free energy of the surface or the number of missing nearest neighbors per unit of area is minimal.

It seems, at first, quite surprising that only three extra spots are observed. The symmetry of the surface layer of nickel atoms on a clean (111) surface of nickel (Fig. 5*b*) has a six-fold rotational axis. As such, both the orientation shown in Fig. 16 and a pyramid rotated 180° with respect to this orientation should be observed. This second form is indeed found under some conditions of growth, but it is not very stable and reverts upon heating to the previously discussed orientation. Actually the normal to a (111) oriented nickel crystal is not a six-fold axis of rotation; it is only a three-fold axis. This is the result of the position of the second layer of atoms with respect to the top layer. Two layers of atoms are required to show the crystal symmetry in this [111] direction. Thus the orientation of the most stable form of NiO is affected by the second layer of nickel atoms as well as by the surface layer. In fact, the orientation and form assumed by such NiO grown on this (111) surface of nickel and probably on the (100) and (110) faces as well, appear to be dependent on at least three geometrical factors. The first, and probably the most important, is the symmetry and dimensions of the surface mesh of the substrate crystal. The second factor is the symmetry of the entire host crystal, and the third is the face of the epitaxially grown crystal that has the fewest number of missing nearest neighbors per square centimeter, or the lowest free energy. Presumably such factors also play an important role in determining the orientation of epitaxially formed layers in other systems.

Summary

This discussion of a few preliminary experiments with nickel points out some of the potential uses of low energy electron diffraction in improving our understanding of many types of surface phenomena. The first, and probably the most basic use, is in the study of clean surfaces. As illustrated in this article, the physical properties of the surface layer of atoms may be totally unlike those in the bulk of the crystal. It is necessary to understand such phenomena before a thorough understanding of chemical effects on surfaces can be achieved. The adsorption of gases, oxidation and corrosion, and the formation of epitaxial layers can all be studied in great detail by low energy electron diffraction.

Probably the most important application of this tool, at least from a standpoint of economics, lies in the field of catalysis. To illustrate the importance of applying new methods of study to catalytic behavior it is worthwhile to quote two sentences from a recent book by Professor Paul H. Emmett (*16*). "The products from processes involving catalysis amount to many billions of dollars in value each year. With all of this industrial emphasis it is perhaps a little surprising that the field of catalysis has remained largely an art up until recent times." Perhaps with the application of low-energy electron diffraction to this and other surface problems, our understanding of surfaces may approach our present understanding of the bulk properties of matter and remove catalysis from the status of an "art."

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