

following equation:

$$[D_{\text{H}^{\text{Nb}}}]_{70} = 1.61 \times 10^{-3} \exp[-0.625/70k] \\ = 3.0 \times 10^{-48} \text{ cm}^2 \text{ sec}^{-1}.$$

The lack of identification of the 70°K hump with the relaxation effect produced by the interstitial hydrogen destroys one of the main analogies<sup>1</sup> between the niobium peak and the dissipation maximum found by Weiner and Gensamer in steel.<sup>5,12</sup> Another difference

<sup>12</sup> The value of  $D_{\text{H}^{\text{Fe}}}$  computed by Weiner and Gensamer from the experimental data concerning the 50°K peak is wrong by a

between the two effects is that the intricate dependence of the peak's height upon aging which has been observed in steel<sup>5</sup> finds apparently no parallel in niobium.

The existence of a relaxation spectrum and the close analogy between the values of  $\bar{W}$  and  $\bar{\tau}_0$  measured in niobium and those found in fcc metals show that, whatever the details of the mechanism may be, the niobium peak is essentially controlled by the dislocations.

factor of 100. The correct value is  $2.8 \times 10^{-16} \text{ cm}^2 \text{ sec}^{-1}$ , and agrees less well with the value  $4.9 \times 10^{-17} \text{ cm}^2 \text{ sec}^{-1}$  obtained from high-temperature experiments.

## Interpretation of Low-Energy Electron Diffraction Patterns of Adsorbed Gases

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Recent observations of the adsorption of oxygen on nickel are interpreted in terms of double scattering processes instead of the single scattering mechanism which has been used in all previous interpretations. This permits a simple explanation of the observed variation of the intensity of the diffraction pattern with electron energy and provides a plausible understanding of the early stages of adsorption.

IN 1927 Davisson and Germer<sup>1</sup> reported diffraction beams due to adsorbed gases along with the results of their classical experiments on the diffraction of electrons by a crystal of nickel. Since then a large number of low-energy electron diffraction investigations of the adsorption of foreign atoms on single crystal planes have been reported, especially by Farnsworth *et al.* To date the interpretation of the experimental results has been based principally upon the assumption that the diffraction pattern associated with the adsorbed atoms is the result of a single direct scattering by the

adsorbed atoms, as demonstrated in Fig. 1(a). Recent observations<sup>2</sup> with missing explanations reveal the inadequacy of this assumption. It is the purpose of this paper to report a new assumption which includes *double scattering*, as demonstrated by Figs. 1(c) and (d). This new assumption provides not only the missing explanations but also more reasonable explanations in the case of other observations.

Recently Germer and Hartman<sup>2</sup> reported the following unexplained observations in the case of oxygen adsorbed on nickel.

*Observation 1.* Good patterns from two-dimensional arrays of adsorbed atoms appear at certain electron wavelengths only. According to the theory of diffraction of plane waves by a plane grating, the diffraction pattern should be observable equally well for all wavelengths smaller than the lattice constant.

*Observation 2.* At very low coverage of approximately 0.1 monolayer, the (10) reflections are streaked in contrast to the diffuse (30) reflections. Furthermore, the (10) reflections are occasionally missing.

*Observation 1* may be accounted for in the following way. The scattering of slow electrons by oxygen atoms is strongly peaked in the backward and forward directions with the former always less than the latter.<sup>3</sup> From accelerating potentials of approximately 50 v on, the backward scattering decreases rapidly with increasing electron energy and the double scattering processes such

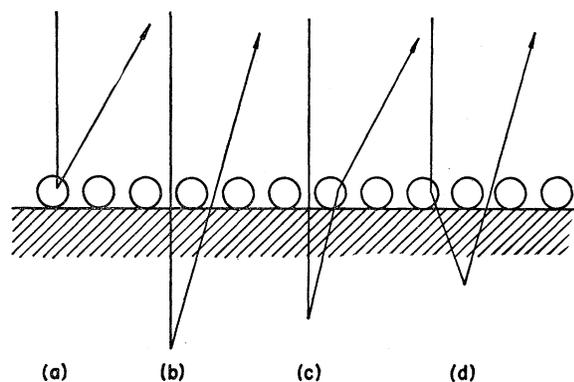


FIG. 1. The different scattering processes: (a) single scattering by gas atoms ("gas beam"); (b) single scattering by crystal ("crystal beam"); (c) double scattering, crystal-gas; (d) double scattering, gas-crystal.

<sup>1</sup> C. Davisson and L. H. Germer, *Phys. Rev.* **30**, 705 (1927).

<sup>2</sup> L. H. Germer and C. D. Hartman, *J. Appl. Phys.* **31**, 2085 (1960).

<sup>3</sup> E. Bauer (to be published).

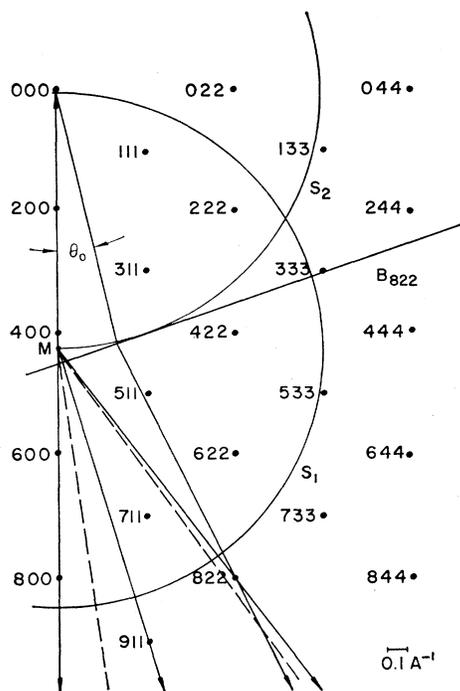


FIG. 2. Reciprocal lattice of nickel (011) plane. Dashed lines: limits of observation in Germer and Hartman's experiment. Primary beam pointing from  $M$  to 000;  $B_{hkl}$  trace of Brillouin zone boundary  $hkl$ ;  $S_1$  trace of Ewald sphere for  $\lambda=0.834 \text{ \AA}$  ( $E=E_0+V_0=200+16 \text{ ev}$ ).

as Figs. 1(c) and (d) become more important. Consequently, in the wavelength regions where strong diffracted beams from the crystal appear, the double scattering process of Fig. 1(c) is more dominant than the single scattering process of Fig. 1(a). The singly scattered waves of Fig. 1(a) and the doubly scattered waves of Fig. 1(c) or the waves scattered three times by a combination of the processes of Figs. 1(c) and 1(d) can interfere constructively.<sup>3</sup> Consequently, the intensity of the "gas beams" will be enhanced in these wavelength regions. This is especially true at higher electron energies (several hundred volts) where the singly scattered waves can be neglected to a first approximation, so that the phase relations between the singly and doubly scattered waves do not have to be considered. Thus, observation 1 is explained.

The explanation of *observation 2* requires some crystallographic considerations. Figure 2 shows one quadrant of the (011) plane of the reciprocal lattice of nickel. Circle  $S_1$  is the section of the Ewald sphere for  $\lambda=0.834 \text{ \AA}$  (216 ev) with this plane. Of the possible reflections (800), (911), and (822) only the reflection (911), or (20) in plane grating indices, is observable in the  $A$  azimuth in Germer and Hartman's experimental arrangement. Because of the large excitation error the reflection is weak compared to the (820) reflection in the  $B$  azimuth, for which the excitation error is approximately zero. No other reflections are observable in any

azimuth for a parallel primary beam. However, with adsorption of gas the primary beam in the crystal is modified by the strong forward scattering of the surface gas atoms [see Fig. 1(d)] and can be represented by a spherical wave the amplitude of which rapidly decreases with increasing deviation  $\theta_0$  from the original primary beam. The possible reflections for a spherical wave are easily determined by intersecting the Brillouin zone boundaries  $B_{hkl}$  with the sphere  $S_2$  of radius  $1/\lambda$  with its center at (000).<sup>4</sup> Figure 2 shows this construction for the reflection (822). It is the only one which fulfills the additional condition that  $\theta_0$  must be small. If a sufficient number of electrons are scattered into the angle  $\theta_0$  then a diffuse reflection (822) is observable at the position of Germer and Hartman's diffuse (30) reflection.

At low coverage the diffraction pattern due to gas therefore consists only of the streaked (21) and (10) reflections. These can be accounted for by assuming two equivalent sets of linear atom arrangements parallel to  $[011]$  and  $[0\bar{1}\bar{1}]$  directions with twice the nickel atom spacing in these directions; the lines of a given set are assumed to be randomly spaced. The diffraction pattern of this structure is a family of hyperbolas, as shown in Fig. 3. The intensity distribution along the hyperbolas is determined by the intensity and direction of the "primary" beams and by the angular distribution of the scattering from the gas atoms. The "primary" beams are very strong (820) beams, weak (911) beams, and a weak (800) beam which may be designated, respectively, as (22), (20), and (00) in two-dimensional notation. The maximum angle at which scattering from the gas atoms is observable can be estimated from the

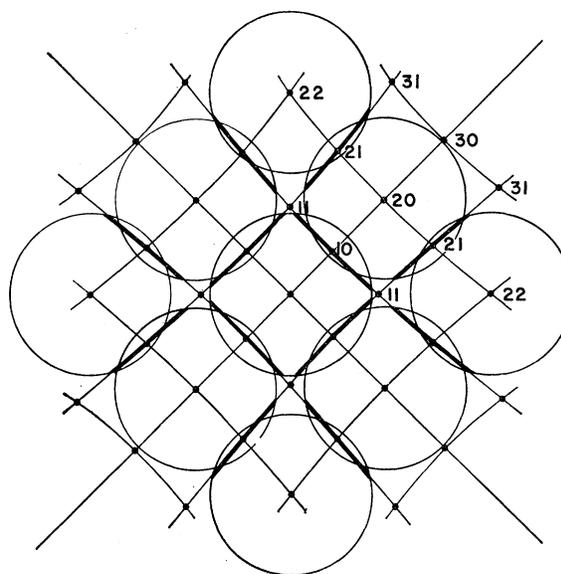


FIG. 3. Diffraction pattern for linear gratings (hyperbolas) and plane gratings (intersections of hyperbolas).

<sup>4</sup> E. Bauer, *Electron Diffraction* (Verlag Moderne Industrie, Munich, 1958), p. 28.

(822) reflection to be approximately  $13^\circ$ . The nearly circular ellipses around the "primary" beams in Fig. 3 correspond to this scattering angle and indicate that only segments of the hyperbolas will be observable. The reflections (20) and (22) do not appear streaked because only a fraction of the corresponding "lattice" beams is scattered by the gas atoms. The maximum length of the segments is determined by the maximum number of atoms which are adsorbed in the linear arrays before the two-dimensional periodic structure starts to develop. As soon as the latter happens, the segments become shorter and contract to spots given by the intersections of the hyperbolas (plane grating pattern). With increased oxygen coverage an increased number of electrons are scattered at larger angles so that the (11) and (31) reflections also become visible with the (820) or (22) beams as "primary" beams. The (820) beams also provide additional intensity for the (10) and (30) reflections. This explains why the (11) and (31) reflections cannot be observed at low coverages (0.3 monolayer). The lack of a clear pattern in the existence range of the two-structure in case of adsorption without warming the crystal can be attributed to a statistical distribution of the oxygen atoms in the potential minima between the nickel atoms corresponding to the four-structure and two-structure arrangement.

The physical arguments for this model are rather strong. Steps on crystal surfaces are preferred adsorption sites. In the fcc lattice the equilibrium steps on a (100) face have  $[011]$  and  $[0\bar{1}\bar{1}]$  directions. The heat treatment used by Germer and Hartman is sufficient to develop the equilibrium form and insufficient to produce any kinetic step structures. The surface is therefore covered by  $[011]$  and  $[0\bar{1}\bar{1}]$  steps, the number of which depends on the pretreatment and heat treatment of the surface. Therefore the intensity and length of the streaked (21) and (10) reflections which are attributed to adsorption along these steps not only varies with the excitation error for the (911) and (800) reflections as determined by direction and wavelength

of the primary beam, but will also vary from one adsorption run to the other.

Besides double scattering by adsorbed gases, which has been shown above to be of fundamental importance in low-energy electron diffraction, another phenomenon may be of importance in the early adsorption stages, namely, preferred adsorption on high-index planes. The chemical and electrolytical etching and polishing techniques used in the preparation of single-crystal surfaces frequently produce not only the crystallographic plane parallel to the geometric surface but also small sub-microscopic facets of other crystallographic planes. These may not be detectable by low-energy electron diffraction from the clean surface because of their small contribution to the total surface. In the early stages of gas adsorption, however, adsorption usually takes place preferably on the facets having the highest free surface energy and these may become observable this way. For example, the four-structure of oxygen on nickel may be qualitatively accounted for (within the observable colatitude range) by adsorption on incomplete  $\{211\}$  planes with the same atomic spacing along the  $[011]$  and  $[0\bar{1}\bar{1}]$  directions as given above. In this case the diffraction pattern due to the four-structure would have to be ascribed to adsorption layers on  $\{211\}$  facets, the two-structure to adsorption on the (100) plane. However, the explanation given above provides a better quantitative fit to the experimental results. In any case, to eliminate such ambiguities, low-energy electron diffraction investigations of adsorption phenomena on single-crystal surfaces should be combined with other techniques, e.g., electron microscopy and diffraction of fast electrons, especially if only a limited colatitude range is observable and no precise intensity measurements are possible. A program along these lines is in progress in this laboratory.

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