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Resonance Effects in Low and High Energy Electron Diffraction by Crystals

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The relation between an anomalous intensity effect in patterns from high energy electron diffraction by crystals, and the so-called resonance effect in LEED, is discussed mainly on the basis of experimental observations with electrons in both energy ranges, using crystals of zincblende, magnesium oxide and gallium arsenide. It is concluded that these two effects are essentially of the same nature. It is pointed out, that the intensity enhancement of the specular spot and other Laue-zone spots, which occurs under conditions of resonance, is particularly conspicuous when the specular spot is also a Bragg reflexion spot. The nature of the wave field generated in the crystal at resonance is discussed in connexion with other phenomena which appear under the resonance condition, such as the overall intensity enhancement of electron scattering, the increase of secondary electron emission and the variation of X-ray emission yield.

1. Introduction

It is well known that there are various kinds of anomalous intensity effects in slow electron diffraction (or low energy electron diffraction, LEED) by crystals, such as those involving diffraction maxima at positions not fulfilling the Bragg conditions, splits of Bragg peaks, significant peak shifts, *etc.*

Attempts to interpret these anomalies have been made by consideration of kinematical or dynamical diffraction theory. For instance, at an earlier stage of LEED studies, MacRae & Germer (1963) explained peak shifts observed for nickel crystals by assuming a change from the bulk value of the spacing of the surface atomic layers. In connexion with experimental observations of off-Bragg peaks, Gerlach & Rhodin (1967) assumed an asymmetric behaviour of surface atoms with respect to the scattering and absorption of electrons. These are examples of the approach from the kinematical theory.

Miyake & Hayakawa (1965, 1966) on the other hand pointed out that most anomalies in slow electron diffraction call for interpretation on the basis of the dynamical theory, and showed experimental examples illustrating dynamical effects, and outlined some theoretical considerations. This point of view implies that most of the anomalous features in LEED are the results of dynamical interactions between many diffracted waves.

Meanwhile, the importance of dynamical effects for slow electrons was gradually recognized (McRae, 1966; Boudreaux & Heine, 1967; Gervais, Stern & Menes, 1968). In particular, McRae presented a new formulation of the theory of electron diffraction, and predicted the appearance of a resonance peak, resonance minima and fractional order peaks (or secondary Bragg peaks). Kambe (1967, 1968), Ohtsuki (1968*b*) and Hirabayashi (1968*a*) also formulated similar theories.

No doubt these theories have some merit with regard to the LEED phenomena. It is obvious, however, that any theory of electron diffraction in a crystal retaining lattice periodicity must be substantially equivalent to the traditional dynamical theory given by Bethe (1928) in so far as they are all based on the theory of potential scattering. It must be remembered in this connexion that the high energy electron diffraction phenomena also involve a number of anomalous effects in diffraction intensities, and many of them have been explained, at least qualitatively, by Bethe's dynamical theory. It is therefore natural to suppose that anomalous effects corresponding to those found for high energy electrons may appear in the same form, or with some small differences, in low energy electron diffraction also. In any case, high energy electron experience should be fully utilized in interpreting the LEED phenomena, in which there seems still to exist some confusion in the theoretical interpretation because of the complexity of the dynamical effect involved.

The present paper describes typical anomalous intensity effects which are well known for high energy electrons, followed by a discussion of the anomalous effects for low energy electrons which have recently been found experimentally or theoretically discussed. Some new observations of low and high energy electron diffraction, from cleavage faces of zincblende, magnesium oxide and gallium arsenide, are also reported.

2. Off-Bragg reflexions in high energy electron diffraction

(*a*) *Kikuchi & Nakagawa's observations*

Kikuchi & Nakagawa (1933) made a detailed study of the behaviour of electron diffraction spots obtained with electrons in the energy range 40$\sim$100 kV from (011) cleavage faces of zincblende crystals, using stationary- and rotating-crystal methods. They found two kinds of intensity anomaly in rotating-crystal diffraction spectra:

(i) A normal Bragg spot often splits into two or more intensity maxima, with features which depend on the azimuthal angle of the crystal. They called this effect the '*first kind of intensity anomaly*', and explained it in terms of dynamical interactions which take place under conditions of simultaneous Bragg reflexion. This phenomenon, therefore, is essentially of the same kind as that known as *Aufhellung* or *Umweganregung* in X-ray diffraction, although in the electron case the simultaneous Bragg reflexions take place more frequently and, as a rule, with stronger dynamical interactions. This effect may sometimes appear as a considerable peak shift.

(ii) The intensity of the specular reflexion is very often suddenly enhanced when the spot crosses a Kikuchi line which runs in a direction oblique to the horizontal Kikuchi lines parallel to the crystal surface. This enhancement gives rise to an off-Bragg reflexion spot in the rotating-crystal spectrum. Kikuchi & Nakagawa called such an effect the '*second kind of intensity anomaly*'. However, the interpretation of this phenomenon was not attempted at that time.

(b) Subsequent studies on the 'second kind of intensity anomaly'

The second kind of intensity anomaly found by Kikuchi & Nakagawa was studied in further detail both theoretically and experimentally by Miyake, Kohra & Takagi* (1954) and by Kohra, Molière, Nakano & Ariyama† (1962), who succeeded in elucidating it at least qualitatively.

* MKT.

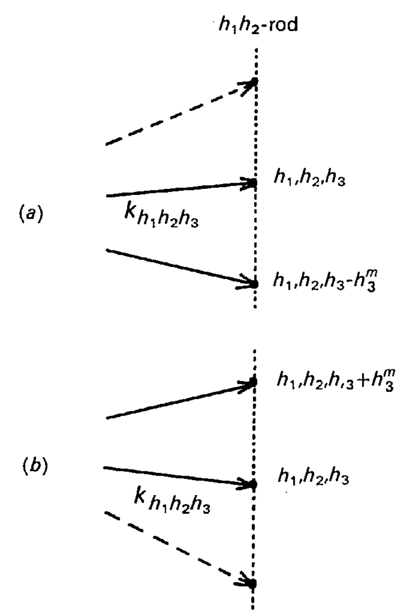


Fig. 1. The situation in reciprocal space for the second kind of intensity anomaly.

MKT pointed out that the overlap of the specular spot on an oblique Kikuchi line usually implies that the incident electrons fulfil the Bragg condition on a certain lattice plane, and that the second kind of anomaly takes place when the reflected wave is propagating in a direction almost parallel to the crystal surface. For example, if the crystal is cubic and the crystal surface is (001), then the surface is the mirror plane of the lattice. If the overlap is with the Kikuchi line $\bar{h}_1\bar{h}_2h_3$, the Bragg reflexion generated has the indices $h_1h_2h_3$.‡ The Kikuchi line concerned does no more than give a convenient indication of the relevant diffraction condition.

That the propagation direction of the reflected wave $h_1h_2h_3$ is parallel or nearly parallel to the crystal surface makes the diffraction problem very peculiar. Such a beam, which may be called the *surface wave*, is generated when the Ewald sphere nearly touches a reciprocal lattice rod h_1h_2, perpendicular to the surface, and the reciprocal lattice point $h_1h_2h_3$ on this rod is in the vicinity of the tangent to the sphere. Strictly speaking, such a diffraction condition corresponds to neither the Bragg nor the Laue case of the usual two-wave problems, but to a case intermediate between the two. Because of this, special considerations are necessary when choosing the appropriate tie-points, as discussed by MKT; KMNA suggested further considerations in this respect from the use of the concept of wave flow in considering the boundary condition. One has, besides, to take into account the following:

(i) Because dynamical interactions between the reflected beam $h_1h_2h_3$ and the lattice plane parallel to the surface will be considerable, the reflected wave $h_1h_2h_3$ will be subject to repeated reflexions of the type $0,0,\pm h_3^m$, where h_3^m is the lowest index h_3 of the non-vanishing reflexion $0\,0\,h_3$, and usually equal to 1 or 2 according to whether the unit cell of the crystal is simple, or face- or body-centred cubic, respectively. Thus simultaneous participation of the planes represented by the reciprocal lattice points on the same rod adjacent to $h_1h_2h_3$ (*i.e.* $h_1,h_2,h_3+h_3^m$ and/or $h_1,h_2,h_3-h_3^m$) is inevitable, as illustrated in Fig. 1. KMNA proved experimentally that the enhancement of intensity of the specular reflexion is appreciable only if the condition

$$2\,|k_{h_1h_2h_3;\,z}| \lesssim h_3^m \cdot |c^*| \qquad (1)§$$

is fulfilled, where c^* is the reciprocal space axis perpendicular to the real crystal surface and $k_{h_1h_2h_3;\,z}$ is the component of the wave vector $\mathbf{k}_{h_1h_2h_3}$|| of the

† KMNA.

‡ For crystals such as zincblende whose cleavage face is (011), the overlap of the specular spot on an oblique Kikuchi line $\bar{h}_1h_2h_3$ implies the generation of the Bragg reflexion $h_1h_3h_2$.

§ The inequality condition in (1) is not very strict.

|| In fact, the wave vector $\mathbf{k}_{h_1h_2h_3}$ inside the crystal cannot be known in advance without a knowledge of the dispersion surface, and in general it may take several values corresponding to a number of tie-points.

reflected beam $h_1h_2h_3$ normal to the surface and directed into the crystal.

(ii) Because of the boundary condition, the reflected beam propagating upwards, whose reflexion indices may be h_1,h_2,h_3 or $h_1,h_2,h_3+h_3^m$ as seen in Fig. 1, cannot emerge from the crystal so long as

$$|k_{h_1,h_2,h_3;z}|,\ |k_{h_1,h_2,h_3+h_3^m;z}| < \sqrt{\frac{8\pi^2 m}{h^2}V_0} \qquad (2)$$

where V_0 is the mean lattice potential of the crystal.

(iii) Relevant tie points may become imaginary which means that the wave-field within the crystal is damped with increasing depth from the surface and cannot penetrate far into the crystal. This situation usually results from (i) even if $k_{h_1,h_2,h_3;z}>0$ so that the diffraction conditions seemingly correspond to the Laue case [Fig. 1(*b*)], as shown by the calculations of KMNA.

Summarizing the work of MKT (1954) and KMNA (1962), the enhancement of intensity of the specular reflexion takes place by excitation of a surface wave related to a reciprocal lattice rod, h_1h_2, the wave field being confined in real space to within a very thin layer near the surface, as the result of a combination of conditions (i), (ii) and (iii). For the emergence of this wave field from the surface, the channel relating to the h_1h_2-rod itself cannot act effectively, the 00-rod related to the specular reflexion usually being the most important of the other rods which may act as possible channels.

The calculations of KMNA, dealing with a four-wave problem for a non-absorbing crystal, showed that the reflectivity of the specular reflexion can sometimes attain nearly 100%. The angular position of the 'off-Bragg reflexion' depends on the azimuthal angle of the crystal. As discussed later, wave fields of the type mentioned above correspond to the so-called localized surface states. The conditions giving rise to this kind of wave field will be called *surface wave excitation.*

(*c*) *Phenomenon of the overall intensity enhancement*

It has been found that, under conditions of intensity enhancement of the specular reflexion, enhancement of the reflexion pattern as a whole occurs, including Laue-zone spots corresponding to each reciprocal rod, temperature diffuse spots and streaks, and the Kikuchi pattern composed of lines and bands (Miyake, 1962; Takagi, 1958; KMNA, 1962; Miyake & Hayakawa, 1968).

Among these, the enhancement of many Laue-zone spots implies the appearance of non-specular off-Bragg reflexions which are rendered through channels relating to rods other than h_1h_2 and 00. Figs. 2(*a*) and (*b*) are diffraction patterns obtained from an (011) cleavage face of zincblende, being a stationary-crystal diffraction photograph at the point of intensity enhancement and a rotating-crystal reflexion spectrum for the same azimuthal angle, respectively, showing the overall features of off-Bragg reflexions. It is of note that non-specular off-Bragg reflexions can be seen on photographs in the paper of Kikuchi & Nakagawa (1933).

3. The 'second kind of anomaly' for Bragg reflexions

Oblique Kikuchi lines make a number of intersections with a horizontal Kikuchi line.* Since, as explained in the previous section, intensity enhancement of the specular spot occurs when it overlaps an oblique Kikuchi line, it is expected that the intensity maximum corresponding to a specular Bragg reflexion $00h_3$ lying on a horizontal Kikuchi line may be further enhanced at these points of intersection.

If the glancing angle is set so that the specular spot lies exactly on the horizontal Kikuchi line $00h_3$, and the azimuthal angle of the crystal is continuously varied, then the specular spot, being now a Bragg reflexion $00h_3$, moves along this Kikuchi line (see Fig. 3). Such a method of observation is similar to that of the Renninger (1937) setting of X-ray diffraction, and has been adopted by Gervais, Stern & Menes (1968) and Stern, Gervais & Menes (1969) in studies of LEED by a single crystal of tungsten. In the following, observations using the Renninger setting in the high energy electron range are described. A discussion of Gervais, Stern & Menes' results is given in a later section.

Fig. 4(*a*)–(*l*) shows a series of diffraction photographs obtained from the (011) cleavage face of a zinc blende crystal with electrons of energy about 100 kV, in which the specular spot satisfies the Bragg condition on 0,10,10 constantly, while the azimuthal angle of the crystal is varied over the range from 80° to 90°, where the angle 90° corresponds to the [0$\bar{1}$1]-azimuth. Fig. 5 shows the whole diffraction pattern for an azimuth in the relevant range. The arrow in each photograph indicates the specular Bragg spot; the spot intensity was estimated by the use of a standard intensity scale.

What is most significant is the fact that the increase in intensity of the Bragg spot at the points of intersection of Kikuchi lines is found to be surprisingly large compared with that for a non-Bragg specular reflexion. In the latter case, the rate of increase in the intensity at the enhancement position is usually of the order of several to ten times; that for the second kind of anomaly for the Bragg specular reflexion may be

* In general, a few oblique Kikuchi lines cross at the same point on a horizontal Kikuchi line.

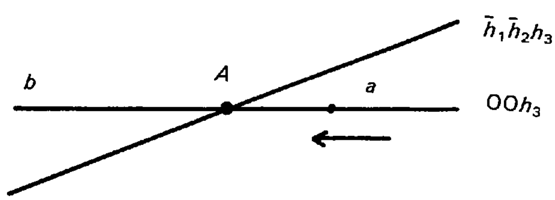


Fig. 3. Point of intersection, *A*, of a horizontal and an oblique Kikuchi line.

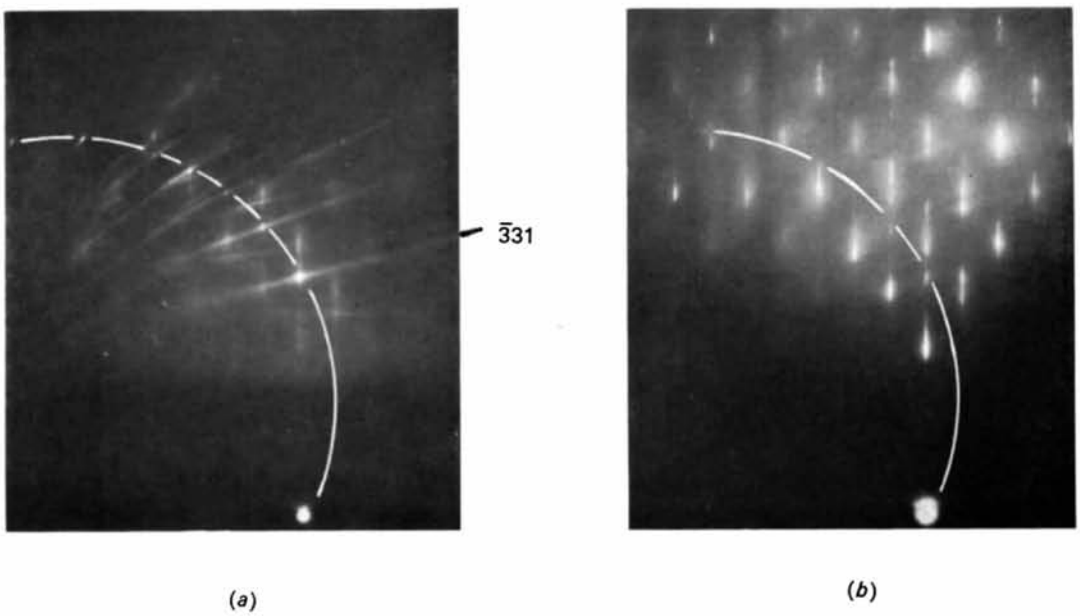


Fig. 2. Diffraction patterns from the (011) face of zinc-blende for the same azimuth, deviating about 2·5° from [0$\bar{1}$1], 100 keV. (*a*) Stationary-crystal pattern, where the arc (drawn with white ink) indicates the location of the Laue zone circle passing through zone spots enhanced by the second kind of anomaly. The specular spot is on the Kikuchi line $\bar{3}31$. (*b*) Rotating-crystal reflexion spectrum containing fractional order reflexions at positions corresponding to the enhanced spots in (*a*).

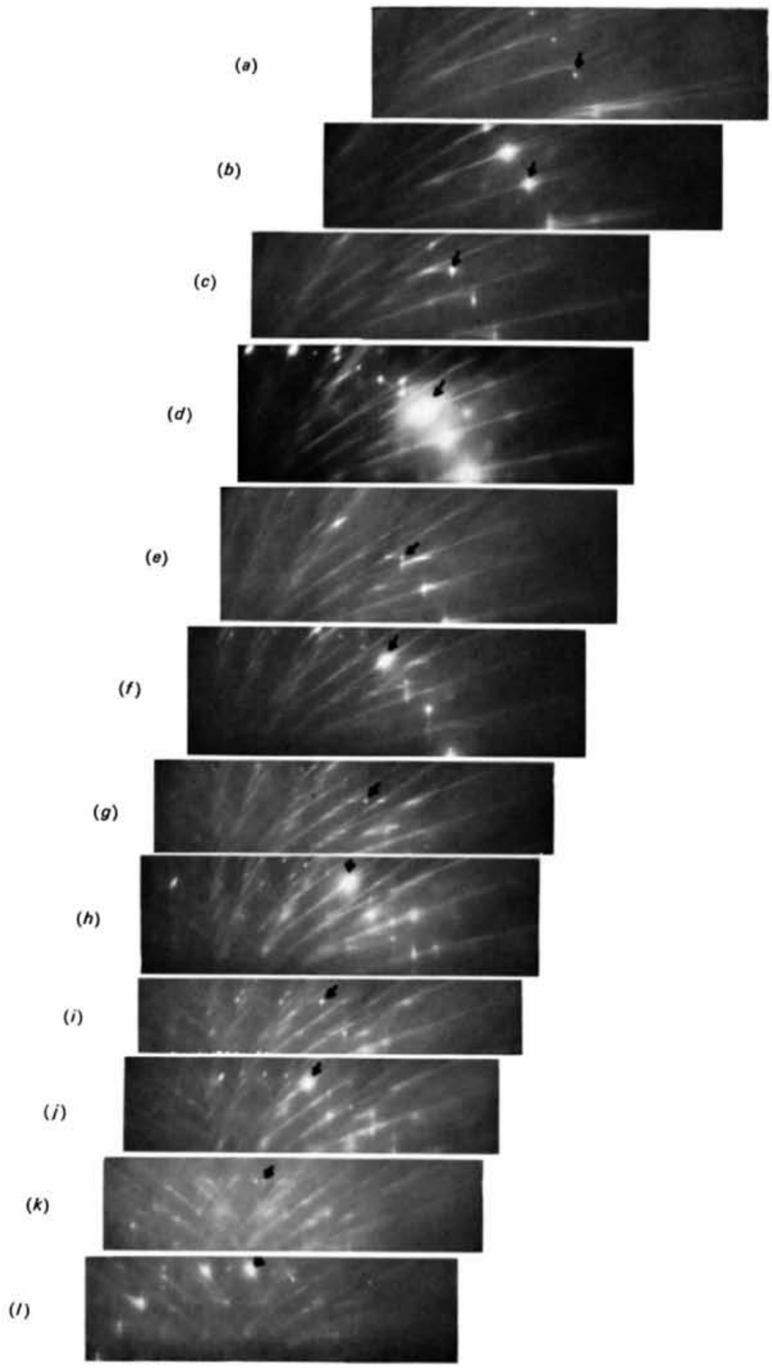


Fig. 4. Intensity variation of the 0,10,10 reflexion, from the (011) face of zincblende, with the change of the crystal azimuth in the range near [0$\bar{1}$1], 100 keV. The specular reflexion (0,10,10-reflexion) is indicated by the arrow. Vigorous intensity enhancements of this and other zone spots are seen in (*b*), (*d*), (*h*), (*j*) and (*l*) due to the second kind of anomaly at each of the points of intersection of Kikuchi lines, whereas their intensities are almost extinguished in, *e.g.* (*e*) compared with (*d*).

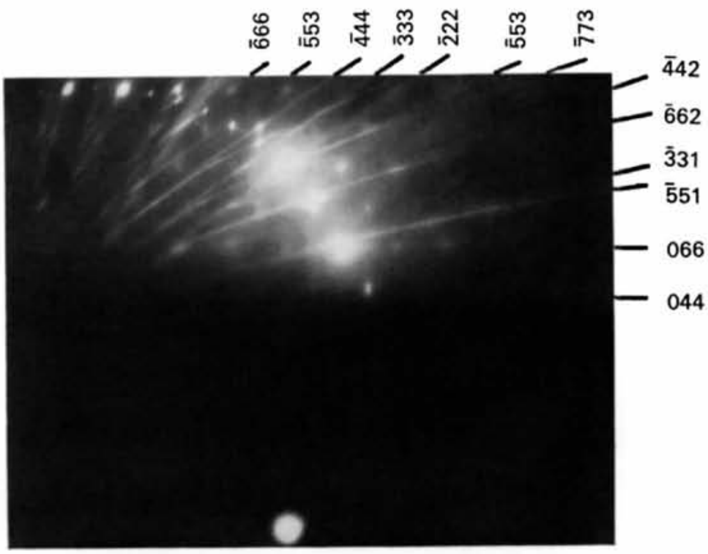
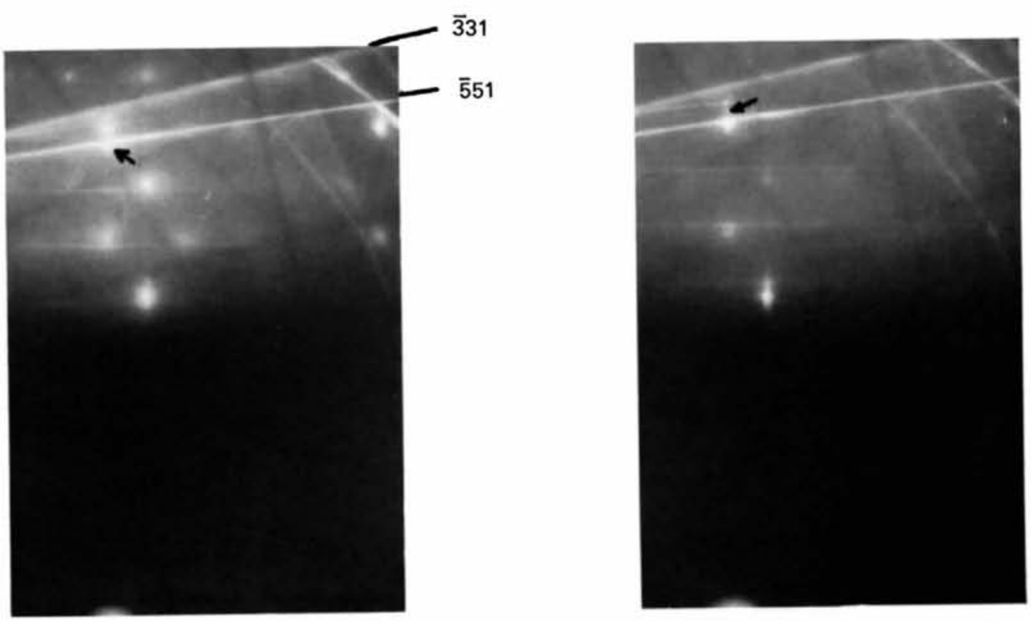


Fig. 5. The whole diffraction pattern corresponding to Fig. 4(*d*), at the azimuth deviating about 2·5° from [0$\bar{1}$1]. Kikuchi lines are indexed.



(*a*) (*b*)

Fig. 6. Example showing the sudden intensity drop of the non-Bragg specular spot (indicated by the arrow) due to the second kind of anomaly; zincblende (011), 100 keV. (*a*) At the enhancement, the specular spot on the Kikuchi line $\bar{5}51$; (*b*) at a slightly deviated condition.

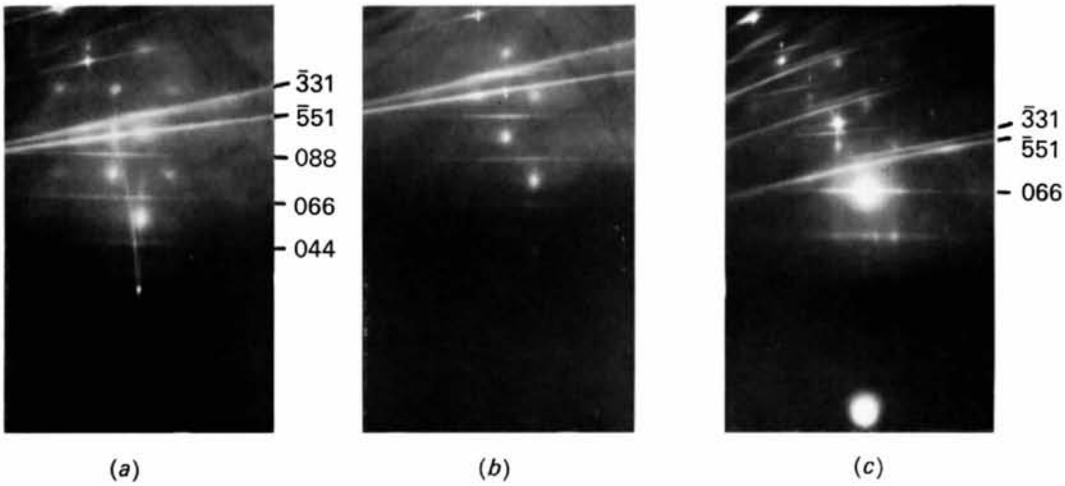


Fig. 7. Circular arcs observed for zincblende, 100 keV. (*a*) At the condition of the second kind of anomaly, the specular spot on the Kikuchi line $\bar{5}51$; (*b*) at a slightly deviated condition from that of (*a*), in which the circle does not appear; (*c*) at the condition of the ordinary Bragg reflexion 066.

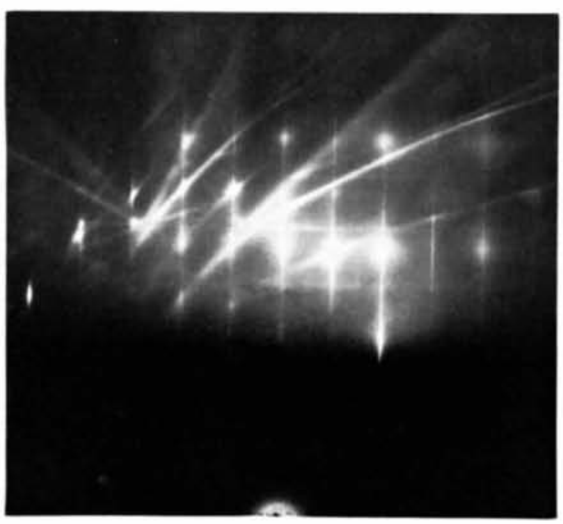


Fig. 8. Diffraction pattern from zincblende at an azimuth deviating a little from [100], showing a number of vertical straight lines, under the condition of the second kind of anomaly; 100 kev.

twenty to thirty times or more. At the same time, considerable excitation of other Laue zone-spots occurs, resulting in fairly strong fractional order reflexions, except the 00-spot which fulfils the Bragg condition.

In a study of temperature scattering in high energy electron diffraction, Takagi (1958) noticed that the non-Bragg specular reflexion behaves asymmetrically with respect to the relevant oblique Kikuchi line. The same trend was observed even more distinctly for the intensity anomaly in the specular Bragg spot. If the part of the horizontal Kikuchi line on which the specular spot (Bragg spot) lies is at the lower-angle side of the relevant oblique Kikuchi line (corresponding to the range *a* in Fig. 3), the intensity of the spot is gradually enhanced as it approaches the point of intersection (the point *A* in Fig. 3), where the intensity maximum is reached. However, when the spot traverses the point of intersection, *A*, so that it is at a position just outside the oblique Kikuchi lines (corresponding to the range *b* in Fig. 3), the spot shows a sudden drop in intensity, and at the same time the other zone spots become almost invisible [see Fig. 4(*c*)–(*e*)]. The intensity of the specular spot then increases again to some extent as it moves still further. Thus, there must exist an intensity minimum at an angle very close to the intensity drop. The intensity peak, the sudden intensity drop and the intensity minimum occur within a very narrow angular range, of the order of several minutes in the Renninger setting method of observation.

When the oblique Kikuchi line involved in the anomaly effect has the indices $\bar{h}_1\bar{h}_2h_3$, the overlap of the specular spot with the point of intersection, *A*, in Fig. 3, implies in many cases the condition

$$K_{h_1h_2;\,z}=0 \tag{3}$$

where $K_{h_1h_2;\,z}$ is the normal component of the wave vector $\mathbf{K}_{h_1h_2h_3}$ ($|\mathbf{K}_{h_1h_2h_3}|=K$, K being the wave number in free space) of the diffracted wave *outside* the crystal, corresponding to the h_1h_2-rod.* It should be noted that this relation, which may be understood on the basis of equation (1) in the paper of KMNA (1962), corresponds to the tangential condition of the Ewald sphere, of radius K, to the h_1h_2-rod. A strong intensity anomaly, therefore, takes place for the specular Bragg reflexion under condition (3). A more detailed consideration of this condition, which is of the same form as that for resonance (McRae, 1966), is given later.

Condition (3) holds approximately for the second kind of anomaly for a non-Bragg specular spot. Fig. 6(*a*) and (*b*) are examples showing the sudden drop in intensity for a non-Bragg specular reflexion. The asymmetrical profile for an enhanced specular spot due to the sudden drop on the higher glancing-angle side of the intensity peak has been predicted theoretically by KMNA (1962) for a non-Bragg case (see Fig. 5 in their paper).

* It should be mentioned that only the points of intersection of a certain set of oblique Kikuchi lines correspond to condition (3). Thus not all the conditions (3) can be found in practice on the basis of Kikuchi pattern diagrams. The use of Kikuchi patterns is convenient as a geometrical guide for the high energy electron case, but not always so with respect to LEED.

4. Circular arc of unknown origin

In diffraction patterns from zinc blende crystals, it is sometimes noticed that a continuous circle appears, passing through the enhanced specular spot and other Laue zone spots. Some examples are shown in Fig. 7. Geometrically, this circle is itself a mathematical Laue-zone circle. It does not belong to the Kikuchi pattern, not being a circular Kikuchi envelope, and in fact it moves, relative to the Kikuchi line system, with a change in the glancing angle or the crystal azimuth. It appears simultaneously with a strongly enhanced spot caused by the second kind of anomaly or with a strong ordinary specular Bragg reflexion. The geometrical condition for its appearance is extremely limited.

For cleavage faces of zinc blende, the continuous circle was observed most often for crystal azimuths in the range near the azimuth [0$\bar{1}$1]. Probably related to this peculiarity of the [0$\bar{1}$1]-azimuth, the diffraction patterns obtained for an azimuthal range near [100] (perpendicular to [0$\bar{1}$1]) sometimes contain, under conditions of the surface wave excitation, a number of straight lines which are normal to the surface, as shown in Fig. 8.

The circle was not observed in crystals of gallium arsenide in spite of its similarity to zinc blende in crystal structure and cleavage. For the magnesium oxide crystal, the circle sometimes appears as seen in Fig. 10(*c*), but only very rarely.

The origin of the above mentioned circular pattern is still unknown, although doubtless its occurrence is closely related to the surface wave excitation; it might be caused by some kind of secondary structure of the crystal surface.*

5. Change of diffraction pattern with electron energy

The features of diffraction patterns of say, 100 eV electrons and those of, say, 50 keV electrons are in fact quite different at first glance, but there is in fact no discontinuity between them. According to observations for electrons over the energy range from 500 to 3000 eV (Hayakawa, Murata & Miyake, unpublished),†

* Strong diffraction spots in the Figures of this paper are often surrounded by a halo [*e.g.* for strong spots in Figs. 5 and 7(*c*)], which is not radially uniform but stronger along the direction parallel to the crystal surface. The fact that it is an interference pattern was confirmed by various means. It appears for zincblende, gallium arsenide and magnesium oxide. The origin of this halo is also unknown. Since its radius is almost the same for different kinds of crystal, it might have a trivial origin such as a substance adsorbed on the surface.

† To be published elsewhere.

the form of the LEED patterns gradually changes with increasing energy, and those for 1000 eV electrons already show almost similar characteristics to those for high energy electrons of, say, 50 keV, with respect to Laue-zone spots, Kikuchi patterns and other kinds of diffuse reflexion.

Enhanced fractional order reflexions as seen in Fig. 2(*b*) also appear when the electron energy is lowered to the LEED range. Fig. 9(*a*)–(*c*) show the intensity curves of the specular reflexion 00 from a cleavage face (001) of magnesium oxide, as functions of the glancing angle, α, of incident electrons of constant energy 1780 eV. The reflexion intensity was measured by use of a Faraday cage and visual or photographic pattern observations were also made where necessary.† From inspection of stationary-crystal photographs, in which Kikuchi lines are observable very distinctly for this electron energy, as shown in Fig. 10(*a*), the crystal azimuth was precisely determined in each case, as indicated in Fig. 10(*c*) as (*A*), (*B*) and (*C*) corresponding to the intensity curves of Fig. 9(*a*)–(*c*) respectively. Fig. 10(*b*) shows, for comparison, a diffraction pattern of 100 kev electrons for approximately the same azimuth as that for Fig. 10(*a*).

By reference to Fig. 10(*c*), it is evident that the extra peak in Fig. 9(*a*), marked by an arrow, is an intensity maximum of the specular reflexion which is caused by the second kind of anomaly, due to the surface wave excitation corresponding to the reciprocal lattice point 204 on the 20-rod. The intensity peaks 008 in (*b*) and 0,0,10 in (*c*) are fairly pronounced, because they nearly fulfil the conditions for the second kind of anomaly for specular Bragg reflexions which were explained in detail in the previous section for high energy electrons. These cases also involve the surface wave corresponding to 204.

Fig. 11(*a*)–(*e*) is a series of intensity curves of the specular reflexion from a magnesium oxide crystal for electrons in the energy range from 500 to 640 eV, at the crystal azimuth deviating about 7° from [010]. The profile of a reflexion peak in each curve varies in a somewhat complicated manner with the electron energy, but all the curves contain very pronounced peaks, *D* and *D'*, in the angular range corresponding to the lowest Bragg reflexion 004. The peak *D'* can be interpreted as an extra peak caused by the second kind of anomaly corresponding to the reciprocal lattice point 202 on the 20-rod. This observation may be most readily understood on the basis of Fig. 10(*c*), where the crystal azimuth concerned is indicated by (*D*). This geometrical condition is also confirmed by observation of the configuration of Kikuchi lines in the diffraction pattern, although they are extremely faint in this case. The position of this extra peak corresponds to the point of intersection of the specular spot with the Kikuchi line $\bar{2}02$. It is to be noted that the peak *D'* shows the feature of a steep drop on the larger angle side. On the other hand, the peak *D* can be interpreted as the 004 reflexion subjected to a large peak shift towards the smaller angles. This interpretation is supported by observations of high energy electron diffraction, in which the configuration of Kikuchi lines in the region near the point *X* in Fig. 10(*c*) is found to be as shown in Fig. 12. A similar situation may also be presumed for the low energy electrons. However, it is probable that the peak *D* is affected at the same time by the second kind of anomaly relating to the 20-rod.

In order to discuss the complicated features of other peaks, a detailed theoretical analysis is necessary for each of them. However, visual observation of the patterns is quite helpful for judging the diffraction conditions in individual cases. For instance, it has been found in this way that, for 560 eV electrons close to the 008 reflexion in Fig. 11(*c*), fairly strong Bragg reflexions 208 and $\bar{2}08$ appear successively with changing glancing angle, when the surface wave corresponding to the 02-rod is also nearly excited. The double 008 peaks in this case seem to be a result of these complicated interactions. Another example of double peaks caused by the combination of the first and second kinds of anomaly is found for the 044 peak from the (011) face of zinc blende with 115 eV electrons, shown in Fig. 12 of a previous paper by the present authors (Miyake & Hayakawa, 1966). In the previous paper these double peaks were interpreted as being due to the first kind of anomaly, but, after scrutinizing the

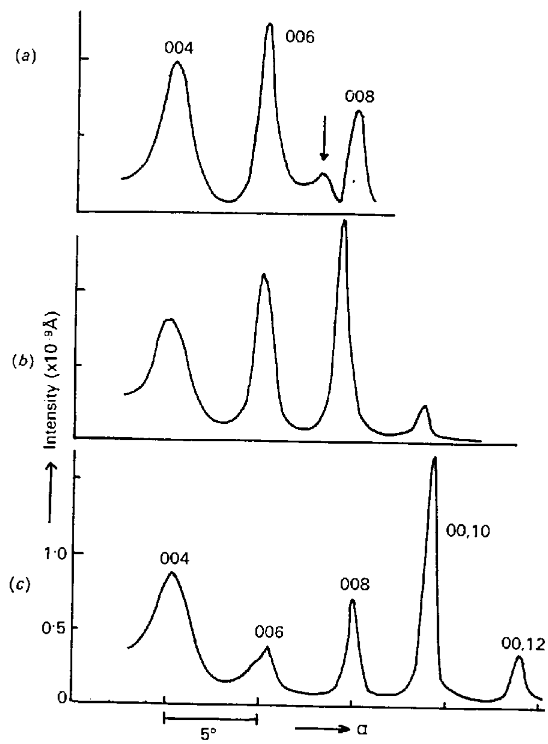


Fig. 9. Intensity curves of the 00-reflexion from the (001) face of magnesium oxide as functions of the glancing angle, α, for electrons of 1780 eV, at azimuths in a range near [010], as illustrated in Fig. 10 for each. (*a*) contains a non-Bragg extra peak indicated by the arrow.

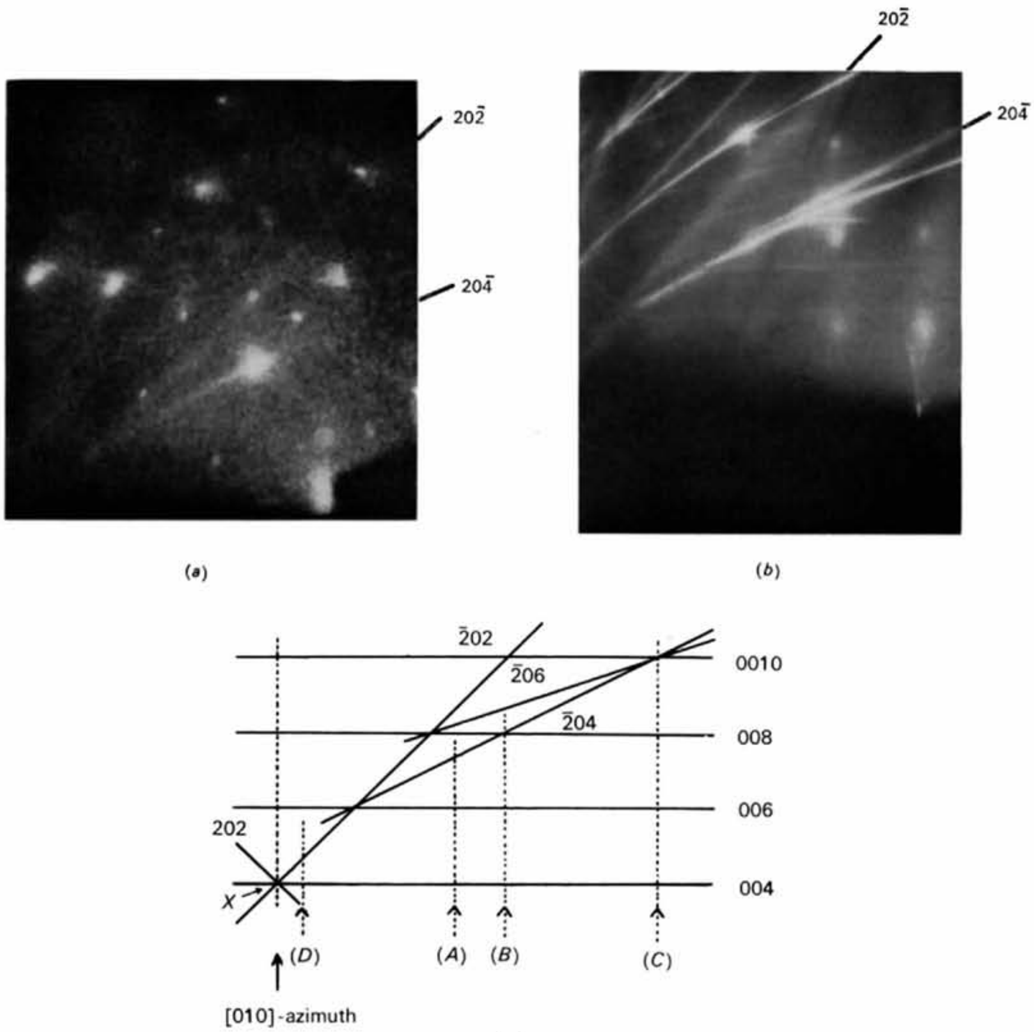


Fig. 10. (*a*) Diffraction pattern for 1780 eV electrons from the (001) of magnesium oxide, at the diffraction condition of the 00,10-peak in Fig. 9(*c*). (*b*) High energy diffraction patterns (100 keV) from magnesium oxide at approximately the same azimuth as that of (*a*). A circular arc (refer to §4) is partly visible. (*c*) Diagram of Kikuchi line configuration, (*A*), (*B*) and (*C*) indicating the azimuths corresponding to Figs. 9(*a*), (*b*) and (*c*) respectively.

diffraction patterns, it is concluded that the first strong peak is caused by the simultaneous participation of the second kind of anomaly.

As already shown the second kind of anomaly is particularly conspicuous for the specular Bragg spot. In connexion with this experimental evidence, it may be meaningful to give an interpretation to the result of Gervais, Stern & Menes (1968, 1969) obtained from a Renninger setting experiment on the (011) face of a tungsten crystal with electrons in the energy range 500–900 ev. As seen in Fig. 13, which is a typical example of their results (1969), they observed that a number of pronounced peaks appeared for the specular Bragg reflexion, (066 in the present example) with changing azimuthal angle. In their second paper, they seemed to decline to attach a more important meaning to the valley regions than to the peak regions, and considered that the valley regions are caused by the simultaneous occurrence of Bragg reflexions in forward directions.

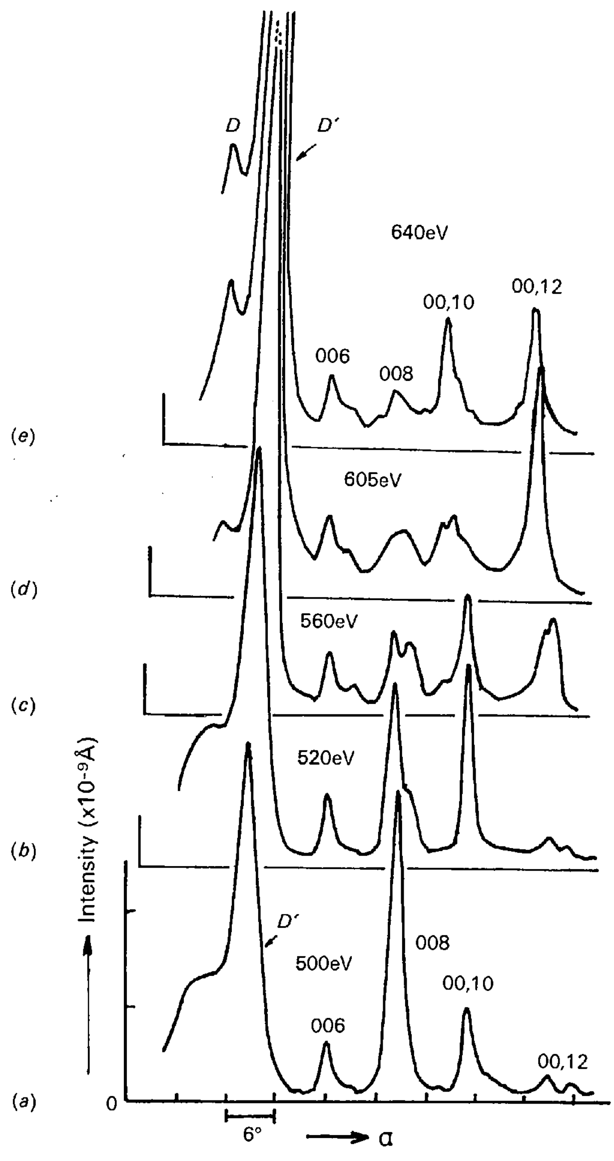


Fig. 11. Intensity curves of the 00-reflexion from the (001) face of magnesium oxide for electrons in the range from about 500 to 640 eV. The crystal azimuth corresponds to (*D*) in Fig. 10(*c*). The peak *D* is the non-Bragg extra reflexion caused by the second kind of anomaly relating to the 20-rod.

The experimental observations on the second kind of anomaly so far described in this paper, however, suggest that the valley regions should be regarded as corresponding to the Bragg reflexions of normal intensities, and that the peaks should again be regarded as being more important. The peaks observed by Gervais, Stern & Menes are undoubtedly those caused by the second kind of anomaly for the specular Bragg reflexions. If we consider the configuration of a set of Kikuchi lines appropriate to their observation, as shown in Fig. 14, then it is at once obvious that the peaks *a*, *c* and *f* in Fig. 13 correspond to the points of intersection *A*, *C* and *F* respectively in Fig. 14. These peaks are due to the surface wave excitation fulfilling condition (3). The above use of a Kikuchi line diagram, however, is given only to clarify the correspondence existing between the effect observed by these workers and that for high energy electrons described in § 3. As mentioned earlier (see footnote in § 3), the use of this kind of diagram is not very satisfactory for determining all conditions for the surface wave excitation, in particular with respect to LEED. Actually, for this purpose there is a more general method using the Ewald construction, and the indices given in Fig. 13 for each peak were obtained by this method, mostly in both triple indices, $h_1h_2h_3$, and double indices (the rod indices) H_1H_2.* They identify the surface wave excitations involved, and it is seen, for example, that the peak *f* is caused by at least two kinds of surface wave. The positions of the peaks found by Gervais, Stern & Menes can be interpreted almost satisfactorily in this way.

6. Types of interactions and corresponding secondary Bragg reflexions

In this section, a survey of the types of intensity anomalies observed for low and high energy electrons is given.

Case A

A non-specular Bragg reflexion may appear when a reciprocal lattice point $h_1h_2h_3$ on the h_1h_2-rod ($h_1, h_2 \neq 0$) falls on the Ewald sphere. However, the second kind of intensity anomaly giving rise to intensity enhancement of the specular spot and other zone spots occurs

* The position of the intersection of a rod with the plane parallel to (011) passing through the reciprocal space origin is given as $H_1\mathbf{a}_1^* + H_2(\mathbf{a}_3^* - \mathbf{a}_2^*)$, where $\mathbf{a}_1^*$, $\mathbf{a}_2^*$ and $\mathbf{a}_3^*$ are the basic vectors of the reciprocal lattice; details of the analysis will shortly be published by one of us (K.H.).

only when the Bragg reflexion excited is a surface wave subject to conditions (1) and (2) in § 2. The intensity enhancement is most marked when the specular spot is a Bragg reflexion.

Case B

The Bragg reflexion $h_1h_2h_3$ not fulfilling conditions (1) and (2) will emerge from the crystal surface as an ordinary Bragg reflexion, or else propagate in a forward direction through the crystal. A similar situation may occur when the specular spot appears as an ordinary Bragg reflexion $00h_3$ while the $h_1h_2h_3$ reflexion is at an off-Bragg position. Intensity enhancement of zone spots may appear in these cases too, but not very strongly, as mentioned later.

Case C

If the specular spot satisfies the Bragg condition for $00h_3$ simultaneously with an ordinary (non-surface wave) non-specular Bragg reflexion $h_1h_2h_3$, the effect expected to appear is the first kind of anomaly in both reflexions.

The above argument may be summarized by the scheme shown in Fig. 15. The secondary Bragg reflexions at fractional order positions appear under the conditions A_1 and A_2 and are particularly conspicuous for A_2, in which, however, the specular reflexion itself is not non-fractional.

For conditions B_1 and B_2 the following was experimentally observed for high energy electrons. When a strong specular Bragg reflexion on $00h_3$ with a low h_3-index takes place corresponding to B_2 (as is the case, for example, for the 044 reflexion from the cleavage face (011) of a zinc blende crystal), then non-specular zone spots are found to be enhanced to a considerable extent, but the effect is generally not so remarkable as that for A_1 and A_2. The same effect is even less marked for B_1.

At least for the high energy electrons, therefore, the secondary Bragg reflexions at fractional order positions are appreciable only by participation of the surface wave excitation corresponding to A_1 and A_2. The same will hold for low energy electrons, although the secondary Bragg reflexions under conditions B_1 and B_2 might be more appreciable than for high energy electrons.

In some cases a complicated diffraction condition involving both kinds of anomaly $A_{1 \text{ or } 2}$ and $B_{1 \text{ or } 2}$ together may occur. Incidentally, the condition derived by McRae (1966) for the occurrence of secondary Bragg peaks is equivalent to that for a non-specular reciprocal lattice point to lie on the Ewald sphere.

7. Discussion

(a) Resonance effects and the phenomenon of the second kind of intensity anomaly

One of the important results of McRae's (1966) theory is the prediction of the appearance of a *resonance peak* in the specular reflexion, and of the *resonance zeros* in all reflexions, for a *two-dimensional crystal* consisting of a single layer of *s*-wave scatterers. He also showed, from theory and a computer calculation, that a resonance peak and *resonance minima* may appear also from a *three-dimensional* crystal.

McRae & Caldwell (1967) carried out LEED experiments on cleavage faces of NaF, LiF and graphite crystals, and concluded that the resonance peak and resonance minimum were experimentally observed as was expected.

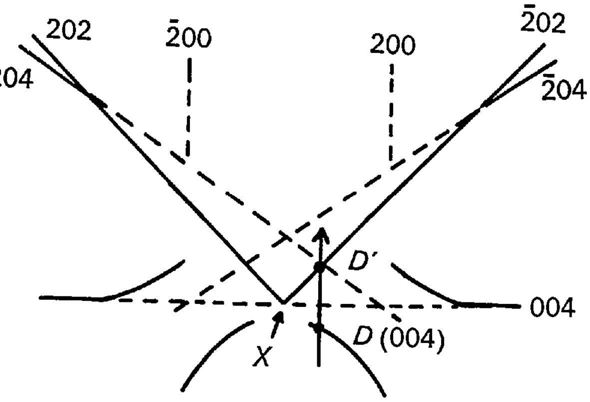


Fig. 12. Kikuchi lines for high energy electrons, in the vicinity of X in Fig. 10(*c*).

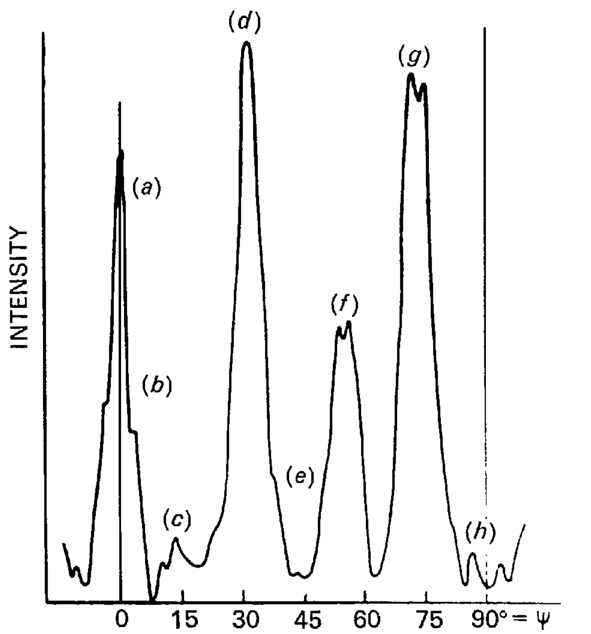


Fig. 13. Intensity variation of 0,6,6 from the (011) face of tungsten with changing crystal azimuth, ψ, (reproduced from Fig. 2 in the paper of Stern, Gervais & Menes, 1969); 825 eV. Indices for each intensity peak specify the surface wave excitations involved. *a*: 060 $(0\bar{6})$, 006 (06); *b*: $(\bar{1}\bar{3})$; *c*: 015 (04); *d*: 242 $(2\bar{2})$; *e*: 215 $(\bar{2}4)$; *f*: 024 (02), $\bar{4}15$ $(\bar{4}4)$; *g*: 233 (20), $\bar{2}24$ $(\bar{2}2)$; *h*: 433 (40).

In their experiment, the intensity of the 00-reflexion was measured as a function of the electron energy for the angle of incidence which was fixed in each measurement. They observed, *e.g.* for NaF, an extra peak to appear at a slightly lower energy than that for the 004 peak, corresponding to the surface wave relating to the rod (say $0\bar{2}$) which is nearest to the 00-rod.* When the angle of incidence was increased, the extra peak moved towards smaller energy values in contrast with the normal movement of ordinary Bragg peaks towards higher energy values.

According to the considerations in the present paper, the extra peak observed in their experiment is interpreted as a special case of the 'second kind of anomaly' caused by surface wave excitation relating to the reciprocal lattice points on the $0\bar{2}$-rod, in particular the lattice point $0\bar{2}2$, as illustrated schematically in Fig. 16. As already pointed out in § 3, the second kind of anomaly takes place exactly, or very nearly, when $K_{h_1h_2;\,z}=0$. This condition is the same as that predicted by McRae for the occurrence of resonance.

As to the resonance minimum, McRae & Caldwell studied the specular reflexion spot from the (001) face of a LiF crystal using a defocused beam for the incident electrons, and found that a line of intensity extinction appeared within the extended area of the spot, corresponding to the diffraction condition under which the Ewald sphere is nearly in touch with the $0\bar{2}$-rod.

By referring to the observations for high energy electrons described in § 3, it is suggested that the theoretical resonance minimum may be closely related to the experimental intensity minimum of the specular spot which takes place on the larger glancing-angle side of the enhanced peak. As already mentioned in § 3, the intensities of zone spots other than the specular reflexion are also suddenly extinguished at the same time. The fact that the sudden drop in intensity and the intensity minimum take place at a glancing angle a little larger than that for the peak is in agreement with McRae's prediction, although his discussion is in terms of the electron energy and not the angle.

As the angular difference between the intensity peak and the intensity minimum near the position of the sudden intensity decrease is only of the order of several minutes for high energy electrons, the condition $K_{h_1h_2;\,z}=0$ has been considered in § 3 to apply to the second kind of anomaly as a whole, *i.e.* the peak, its sudden decrease and the minimum. However, a more detailed examination of this condition is worth while. Strictly speaking, the statement in § 3 that the overlap of the specular spot with the point of intersection of the horizontal Kikuchi line with a certain oblique Kikuchi line (the point A in Fig. 3) in a real diffraction pattern corresponds to the condition $K_{h_1h_2;\,z}=0$ is not correct, because Kikuchi lines in the real pattern are subject to the refraction effect. If we imagine the configuration of Kikuchi lines to be free from refraction, then they will appear at angles slightly displaced upwards (perpendicular to the crystal surface) relative to those in a real diffraction pattern. An exaggeration of this situation is shown in Fig. 17, where the broken lines are the imagined Kikuchi lines and the solid lines the real ones. The point of intersection of the imagined Kikuchi lines, A', is the point which corresponds exactly to the condition $K_{h_1h_2;\,z}=0$.

* Rods including reciprocal lattice points of odd indices may be disregarded for crystals such as NaF. Incidentally, the indexing of two-dimensional diffraction spots in the present paper differs from that of McRae & Caldwell. The indices $0\bar{2}$ in our system correspond to $\bar{1}\bar{1}$ in theirs.

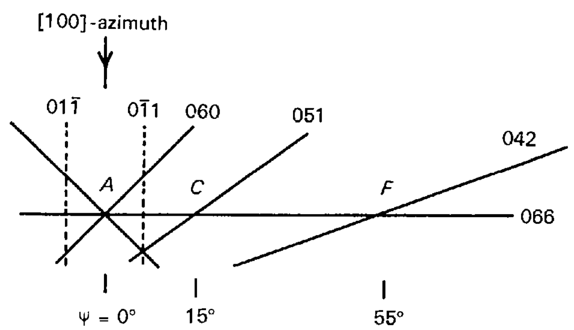


Fig. 14. Kikuchi line configuration in the region near the [100] azimuth for the diffraction condition from the (011) face of tungsten. Only important Kikuchi lines are drawn.

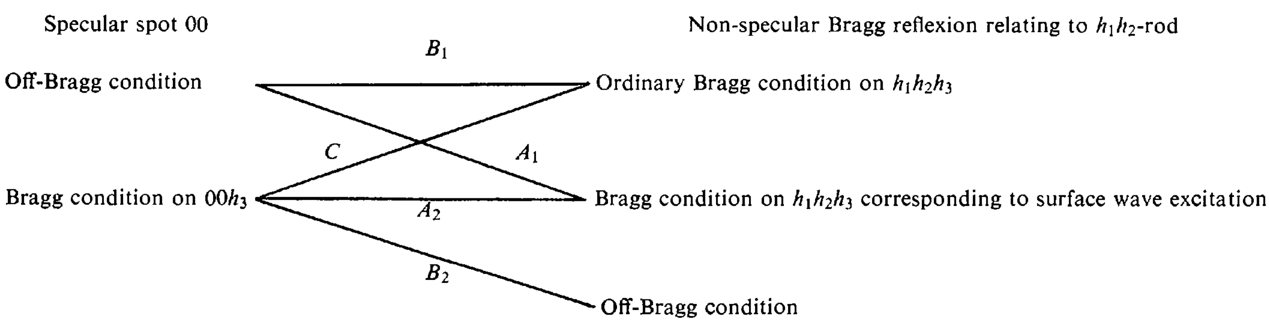


Fig. 15. A_1: the second kind of anomaly, accompanied by secondary Bragg reflexions.
A_2: the second kind of anomaly, accompanied by secondary Bragg reflexions with considerable intensities.
B_1, B_2: may be accompanied by secondary Bragg reflexions to some extent.
C: the first kind of anomaly.

Let us now consider, that the glancing angle of incident electrons is increased at a fixed crystal azimuth in such a way that the specular spot moves upwards along the line AA'. According to the observations for high energy electrons, it has been shown that the intensity peak appears nearest to A, with the sudden drop in intensity a little further away and then the intensity minimum. The point A' corresponds, according to the theory (McRae, 1966), to the condition where resonance ceases, or alternatively speaking, it corresponds to the position where resonance begins. On this basis the detail of the second kind of anomaly may be pictured as shown schematically, with some idealization,* in Fig. 17, where r indicates the whole resonance range, a the range of intensity enhancement in the vicinity of A, b the position of the sudden intensity drop and c the range containing the intensity minimum. The length of AA' corresponds to the angular distance which is appropriate to the mean inner potential.

The above consideration mainly concerns the second kind of anomaly for a specular Bragg reflexion, but the same also applies approximately to the anomaly for a non-Bragg specular reflexion.

From the above discussion, it may be supposed that if the LEED experiment using a defocused beam were performed under ideal conditions, then the extinction line in the specular spot should have an asymmetric profile with very strong intensity on one side. Such a feature, however, is not very clear in McRae & Caldwell's observation.

Finally, it is worth pointing out that, since at the condition for the intensity minimum, all elastic scattering is almost extinguished as observed experimentally, it should correspond to a condition of minimum absorption. This reasoning is in accord with McRae's consideration that the effective field at each atom in the crystal is a minimum under this condition. It is very probable, therefore, that the minimum absorption in this case is of a more anomalous nature than that expected for an ordinary single Bragg reflexion.

(*b*) *Comments on various interpretations*

From the foregoing sub-section, it will be already very clear that the resonance effects predicted by McRae (1966) for LEED and the second kind of intensity anomaly found by Kikuchi & Nakagawa (1933) in high energy electron diffraction are essentially the same phenomena.

Theoretical interpretations of the relevant effects have recently been given independently by Ohtsuki (1968*a*) and Hirabayashi (1968*b*) from approaches a little different from that of McRae. Ohtsuki and Hirabayashi's theories have in common that they consider the coupling between wave functions for one-dimensional effective potentials, corresponding to reciprocal lattice rods perpendicular to the crystal surface. Each of these functions may be called a *rod wave function*. They considered that the resonance effects are caused by the coupling between, say, the 00-rod wave function and another rod function which is in a localized surface state, or the so-called Tamm surface state.*

This kind of approach gives a helpful picture for understanding certain aspects of the second kind of intensity anomaly, or the resonance effects. In fact, as pointed out in § 2 the condition giving rise to the second kind of anomaly is the generation of a wave field which can exist only near the crystal surface, as a result of the conditions (i), (ii) and (iii). Such a wave field is obviously related to the localized surface states of a rod wave function. Hirabayashi suggested that the resonance minima in the specular reflexions are caused by the above mentioned coupling, and that the resonance peaks correspond to intensity maxima which may appear between adjacent resonance

* Curving of Kikuchi lines in the vicinity of the point of intersection is disregarded.

* In order to avoid confusion, the localized surface state should be distinguished distinctly from the simple bound state. The latter may be a continuation of a wave field outside the crystal, while the former may not.

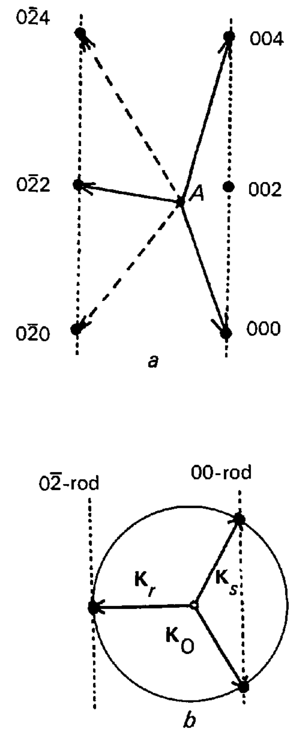


Fig. 16. (*a*) Scheme of the surface wave excitation for one of the possible tie-points, A, in reciprocal space; (*b*) The corresponding wave vectors in free wave space, assuming the exact resonance condition, where $\mathbf{K}_0$, $\mathbf{K}_s$ and $\mathbf{K}_r$ ($|\mathbf{K}_0|=|\mathbf{K}_s|=|\mathbf{K}_r|=K$) are the wave vectors for the incident wave, the specular reflexion and the $0\bar{2}$-rod wave, respectively. (The rod wave outside the crystal first begins to appear when the Ewald sphere touches the rod.)

minima, although the characteristic feature of the intensity peaks which are so conspicuous and sharp was not explained. Experimentally speaking, the intensity maxima are a more remarkable feature of the second kind of anomaly than the intensity minima.

Boudreaux & Heine (1967) dealt with a similar problem in LEED by a 'band theory treatment'. (It should be noted that Bethe's dynamical theory is substantially a band theory.) The wave functions inside the crystal which they assumed, however, seem too simple to explain the details of the resonance phenomena which are of a fairly involved nature. Furthermore, the jump of the mean inner potential at the crystal surface, which is very important in dealing with the 'matching formalism', that is to say the treatment based on the boundary conditions at the surface, was not taken very seriously into account.* Without the potential jump, the localized surface state of a rod wave function is not always ensured. No doubt, however, the application of the advanced results of the band theory should be very helpful in interpreting the electron diffraction phenomena,† in particular with respect to the LEED experiment performed with electrons of varying energy at a fixed direction of incidence [see also *e.g.* Capart (1969)].

As pointed out in a previous paper (MKT, 1953), it is not likely that the second kind of intensity anomaly will occur in X-ray diffraction. This reasoning is related to the existence of the potential jump at the crystal surface for electrons. For X-rays, not only is the scattering cross section very small but the refractive index of the crystal is in general less than unity, in contrast with the electron case for which the refractive index is greater than unity, corresponding to the positive value of the mean inner potential. Because of this, the relation corresponding to (2) in § 2 cannot hold in the X-ray case.

(c) The phenomenon of overall intensity enhancement

The overall intensity enhancement quoted in § 2 is a phenomenon which is still not thoroughly elucidated. Qualitatively speaking, however, it may be understood as follows.

As indicated by KMNA (1962), the wave field within the crystal under the condition of surface wave excitation takes the form of a stationary wave with respect to the direction perpendicular to the surface, with period equal to the shortest spacing between the atomic layers parallel to the surface [corresponding to situation (i) in § 2(*b*)]. It is probable that there is a diffraction condition under which the loop (anti-nodal) planes of the stationary wave coincide with these atomic planes, so that the cross section of each atomic plane for inelastic as well as elastic scattering may increase, even more effectively than expected under the condition of the *n*th order specular Bragg reflexion for which $n \neq 1$. Further, the fact that the wave field concerned involves a period equal to the lattice period parallel to the surface will make this trend more marked. However, at the same time the depth of penetration of electrons within the crystal becomes very small, so that a trend to reduce the total scattering cross section of the crystal as a whole for electrons should result. Thus there are two opposing trends in the scattering efficiency of the crystal. In addition, one has to take into account that the absorption of electrons in the crystal is very large so that electrons scattered well into the crystal cannot reappear at the surface. From these considerations, it may be probable that overall intensity enhancement takes place eventually, under conditions very near but probably just before the resonance maximum. The intensity enhancement of the secondary electrons observed by Stern, Gervais & Menes (1969) under the same diffraction conditions will be explained in a similar way.

A study of the emission yield of Zn $K\alpha$ radiation from (011) cleavage faces of zinc blende crystals (Miyake, Hayakawa & Miida, 1968) revealed that the X-ray emission yield shows remarkable dips under the conditions of the second kind of intensity anomaly and also at ordinary specular Bragg reflexions such as 044,

* If we imagine the excitation of a surface wave, disregarding the potential jump, we have a wave field outside the crystal which is also parallel to the surface. Such a wave field, however, will disappear if the potential jump is taken into account. Incidentally, their statement that 'he (Bethe) represented the wave function inside the crystal by a *single* Bloch wave' is not correct. For instance, Bethe's treatment of a two-wave problem took account of two Bloch waves, and thus, it gave the same intensity profile of a Bragg peak as that shown in Fig. 3 of Boudreaux & Heine's (1967) paper.

† In one of the earliest papers dealing with the electron diffraction problem by an approach based on the band theory is that by Kikuchi (1935).

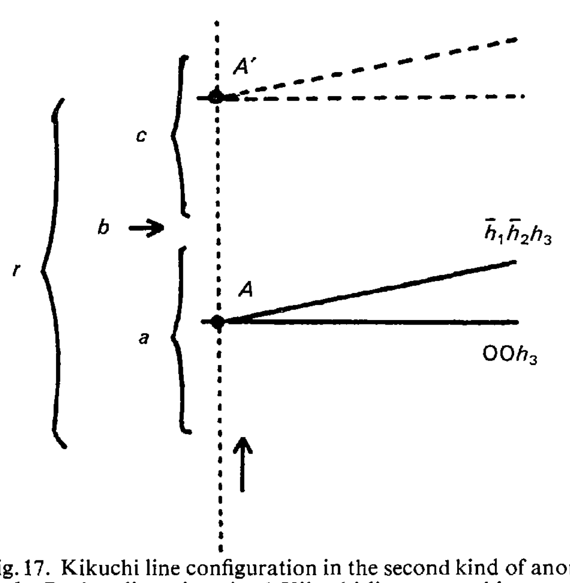


Fig. 17. Kikuchi line configuration in the second kind of anomaly. Broken lines, imagined Kikuchi lines not subject to refraction; Solid lines, real Kikuchi lines subject to refraction. *r*, the resonance region, *a*, the region of enhancement, *b*, the sudden drop and, *c*, the region containing the intensity minimum.

066 *etc.*, and that the yield behaves asymmetrically with respect to each dip, in such a way that the emission yield is stronger on the higher angle side of the dip in the former case, and on the lower angle side in the latter case. This difference in asymmetry between the two cases is probably due to the variation in the depth of penetration of electrons over the above range of diffraction conditions.

The extinction distance corresponding to an ordinary Bragg reflexion is usually of the order of a few tens of Ångströms, whereas that in the case of the second kind of anomaly may become as small as several Ångströms as pointed out by KMNA (1962). Such a small depth of penetration is expected to begin to occur at the lower angle side of the peak, whereas the higher angle side is near the minimum absorption condition [§ 7(*a*)]. It is conceivable that such a large latitude in the depth of penetration under the resonance condition is a determining factor in making the emission yield of X-rays follow this variation approximately.

On the other hand, if, as in the case of an ordinary Bragg reflexion, the variation of the depth of penetration is not so drastic, then the trend due to the variation of the emission yield for each atomic plane also becomes important, and this may result in the opposite asymmetrical features around the intensity dip, as discussed in the previous paper (Miyake, Hayakawa & Miida, 1968). For X-rays, the absorption is negligible so long as the effective depth of excited atoms is less than the order of one hundred Ångströms.

The above qualitative consideration concerning the phenomenon of the overall intensity enhancement and some related effects should of course be confirmed by a detailed theoretical treatment. In any respect, however, quantitative observations of electron scattering and X-ray emission will be valuable in order to pursue the peculiar nature of the wave field under the resonance condition.

8. Conclusion

The primary purpose of the present paper is to emphasize the importance of the comparative study of both the high and low energy electron diffraction phenomena, in order to reach a deeper understanding of the electron diffraction phenomena in general. This importance may be realized by the example presented in this paper, in which it is shown that the 'second kind of intensity anomaly', which was found in high energy electron diffraction as early as more than thirty years ago, is closely related with the LEED phenomena of recent interest called 'resonance effects', and that both phenomena are to be interpreted as essentially the same effect.

It is also shown how knowledge about high energy electron diffraction and about LEED combine very effectively to elucidate a number of effects observed in the respective fields. It is rather striking that so far no such effect has been found which is peculiar only to LEED or to high energy electron diffraction. However, in LEED, particularly for the energy range below 100 eV, a complex situation may be unavoidable owing to the large scattering cross section of electrons, or, in other words, to the simultaneous participation of many reciprocal lattice rods of low indices because of the small radius of the Ewald sphere, as pointed out in previous papers (Miyake & Hayakawa, 1965, 1966).

For detailed discussion of individual features of, say, an intensity curve, it is necessary to deal with a theoretical calculation taking account of a considerable number of diffracted waves, which will in any case require the use of an electronic computer. However, for this purpose it is thought that the machine time will be of the same order whatever the diffraction theory adopted. It is, in this respect, likely that the use of Bethe's form will retain its merits, compared with other formulations.

The authors are grateful to Professor K. Kohra, the University of Tokyo, with whom one of us (S.M.) had a number of occasions of discussing problems relating to the subject of the present paper for many years.

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