On the Inner Potentials of Graphite and Molybdenite.

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ABSTRACT.

Precise values of mean inner potential of graphite and molybdenite were determined by analysing cathode ray reflection spectra. They were found to be 13.0 volts for graphite and 19.5 volts for molybdenite. The apparent decrease of inner potential in low order reflections, which was first observed by Yamaguti, was studied experimentally in detail and compared with the theoretical values calculated by Bethe's theory.

Introduction.

The mean inner potentials of graphite and molybdenite were determined by the method of cathode ray reflection by Yamaguti and others. Yamaguti observed the apparent decrease of the values in low order reflections and Laschkarew suggested that it is caused by the periodic field of potential in the crystal. Laschkarew, Yamaguti and Miyake proposed potential models of the tooth-valley type and explained the observed values in the cases of molybdenite, iron pyrite and zincblende respectively. Kikuchi calculated the effect for nickel using the atom form factor instead of the potential model, but experimental data for the test of his result were not available.

In the present paper, precise values of the inner potential for graphite and molybdenite are determined experimentally, and they are compared with those calculated by Bethe's theory of cathode ray diffraction.

Apparatus.

The experiment with graphite was carried out with the apparatus used by Yamaguti. Later the system of long slits was substituted.

by pinholes and the crystal holder was improved so that the crystal could be rotated about the axis normal to its surface through a ground joint. The experiment with molybdenite was carried out with the improved apparatus. The beam accelerating voltage was about 40 kv. and the total electron current was 0.1~0.5 mA. Rotation photographs were obtained with the exposure of about two minutes under these conditions.

Analysis of rotation photographs.

The method of calculating inner potential by the analysis of rotation photographs was the same as that described by Yamaguti(1); namely the apparent inner potential $E_n$ which corresponds to the $n$th order of reflection, was calculated by the modified Bragg relation

$$\mu_n^2 - 1 = -\sin^2 \theta + \frac{n^2 \lambda^2}{4d^2} \quad \ldots \ldots \ldots \ldots (1)$$

and the formula

$$E_n = (\mu_n^2 - 1) \frac{\hbar^2}{2me\lambda^2} \left(1 + \frac{\hbar^2}{mc^2\lambda^2}\right)^{-\frac{1}{2}}, \quad \ldots \ldots \ldots \ldots (2)$$

where $\epsilon, m, c, \hbar, \lambda, d$ and $\theta$ have their usual meanings and $\mu_n$ is the refractive index of the crystal for cathode rays. $\mu_n$ and $E_n$ are not constants, but depend on the order of reflection $n$.

Experimental results.

Graphite. An example of the spectrum due to a cleavage plane is reproduced in Fig. 1. Many sharp rings superposed on the spectrum were used to check the wave-length of cathode rays. Twelve rotation photographs, which do not show the first anomalous effect described by Kikuchi and Nakagawa(2), were analysed. The mean values of $E_n$ and their experimental errors are given in Table I and plotted in Fig. 3. The mean inner potential determined from the asymptotic value of $E_n$ is 13.0 volts.

Molybdenite. In the experiment with this crystal, the azimuthal setting of the crystal was determined accurately. We define the azimuth where the plane of incidence is parallel to [10i0]-axis as $\varphi = 0$. A number of rotation photographs due to the cleavage face were obtained at different $\varphi$, one of them being reproduced in Fig. 2a. The first anomalous effect of Kikuchi and Nakagawa is observed in many photo-

(1) I.e.
graphs. In some cases it is so remarkable that short Kikuchi lines are visible even in such rotation photographs.

Only those photographs which do not show the effect must be used for the analysis; however the disturbance of the effect was observed at every azimuth for reflection of orders \( n > 17 \). \( E_n \)-values for \( n > 17 \) calculated from different photographs do not coincide. It is not due to the experimental error caused by the weak intensity of the reflection spots, but due to the anomalous effect. \( E_n \)-s for \( 5 > n > 16 \) were calculated from twenty photographs obtained at azimuths \( 8^\circ > \varphi > 17^\circ \) and \( 22^\circ > \varphi > 16^\circ \), where the disturbance of the effect is rather small. \( E_n \)-s for \( n = 3, 4 \) were calculated from five photographs, because such low order reflections, on account of their very small angles, appear only when the surface of crystal is not curved. \( E_n \)-s obtained in this way are shown in Table II and plotted in Fig. 4. The value of the mean inner potential is determined to be 19.5 volts.

The order of reflections, especially for very low orders, were determined by the following method. A cleavage surface was heated fifteen minutes in an electric furnace at about 600°C, it was dipped in ammonia solution to remove the oxide (MoO\(_3\)) produced on the surface.
and then washed with distilled water. The refraction effect is decreased for such specimen, and the lower order reflections appear very clearly. The order was determined by comparing the two spectra due to the treated and the untreated surfaces. (Fig. 2b).

The forbidden reflections, as observed by Reather\(^{(1)}\), are expected theoretically for this crystal when \( \varphi = 0 \), but they were not observed with the untreated cleavage surface, because the second anomalous effect described by Kikuchi and Nakagawa\(^{(2)}\) is very remarkable at this azimuth. The disturbance due to the effect is reduced in the treated surface and the forbidden reflections appear beautifully. Their intensity is comparable with that of the ordinary reflections when \(| \varphi | < 3^\circ\).

**Calculation of the decrease of inner potential in low orders.**

According to Bethe's theory, \( E_n \)'s when calculated turn out to be

\[
E_n = E - \frac{V_{11}}{1 + \frac{d}{4\pi\hbar} T}, \quad \ldots \ldots \ldots \ldots \ldots \quad (3)
\]

where \( E \) is the mean inner potential, \( d \) is the spacing of reflecting net plane which is parallel to the surface, and \( V_{11} \) and \( T \) are given as

\[
V_{11} = \sum_{\mathbf{g}}' \frac{v_{\mathbf{g}}^2}{\kappa^2 - k_{\mathbf{g}}^2}, \quad T = - \sum_{\mathbf{g}}'' \frac{4\pi(n_0)}{(\kappa^2 - k_{\mathbf{g}}^2)^5} (\varphi_{n_0}^2 + \varphi_{n_0}^2) \quad \ldots \ldots \ldots \ldots \quad (4)
\]

where \( v_0, \kappa, k_0, \mathbf{g} \) and \( n \) has the same meaning as those in Bethe's paper. We shall assume hereafter that the unit translations \( a_1 \) and \( a_2 \) are parallel to the surface and \( a_3 \) is normal to it. \( \sum'' \) then means

\(\:
(1)\ 1.e.
(2) H. Raether: Z. Phys. 78, 527 (1932).
triple summation with regard to \( q(g_1 g_2 g_3) \), where (000) and (00h) are omitted. The formula (3) holds when the correction term \( (d/4\pi h) T \) is very small compared to unity. It is also assumed in deriving (3) that the voltage of cathode rays is very large compared with \( E \), which is always satisfied in the case of fast electrons.

The second term in (3) is caused by multiple scattering of cathode rays in crystals, and it depends on \( v_0(q4000) \), namely the form of periodic potential field. The phenomena corresponding to this term, which are scarcely observed in the field of X-rays, were considered to be anomalous when they were discovered. \( V_{11} \) is divided into two parts as

\[
V_{11} = \sum_{g_1 v_1}^{+} \sum_{g_2 v_2}^{0} \sum_{g_3 v_3}^{0} v_0^2,
\]

The first summation is only appreciable when another reflections take place simultaneously with (00h) reflection. The first anomalous effect of Kikuchi and Nakagawa is explained by this term. Care must be taken of the disturbance due to this effect, which is expected to be especially large at rational azimuths, in the determination of inner potential from the rotation photographs.

The second summation, which does not depend on azimuth, explains the anomalous effect observed by Yamaguti. When the first term is neglected, \( V_{11} \) and \( T \) are given as

\[
V_{11} = \left( \frac{a}{2\pi} \right)^2 \sum_{g \neq 0} v_0^2, \quad T = \left( \frac{a}{2\pi} \right)^2 \sum_{g \neq 0} \frac{h}{g^2(h-g)} v_0^2, \quad \text{(4')}
\]

where \( v_0 \) is given by

\[
v_0 = 2 \frac{a^2e}{\pi} \frac{1}{V} \frac{Z_v - F_v}{g^2}, \quad \text{(5)}
\]

where \( Z_v \) and \( F_v \) are the crystal structure factors for nuclear charge and electron cloud respectively, and \( V \) is the volume of unit cell.

**Numerical calculation.**

Graphite. \( Z_v \)'s at 0°C calculated from the structure of this crystal were corrected by the Debye factor \( e^{-\frac{\theta}{T}} \), calculated by Waller's formula taking the characteristic temperature as \( \theta = 1270^\circ \text{K} \). \( F_v \)'s at room temperature obtained by Lonsdale \( \text{(3)} \) from the intensity of X-ray reflection were adopted. \( v_0, V_{11} \) and \( T \) calculated by (4) and (5) are given

(1) I.c.
(2) International crit. tab. V. 95.
in Table I \( E_g \)'s were calculated by (3), where for the value of \( E \) the experimental value 13.0 volts was used\(^{(1)}\). They are given in the last column of the table and plotted in Fig. 3.

**Molybdenite.** \( E_g \)'s were calculated as in the case of graphite, where for the parameter of this crystal the value obtained by Yamaguti\(^{(2)}\) was used. \( F_g \)'s were obtained from the atomic scattering factors \( f \) of non-ionised Mo- and S-atoms. The Debye factor was neglected, because the characteristic temperature of this crystal is unknown. \( \nu_0, V_1, T \) and \( E_g \)'s calculated as in the preceding case are given in Table II and \( E_g \)'s are plotted in Fig. 4.

**TABLE I** Graphite.

<table>
<thead>
<tr>
<th>( n ) or ( g )</th>
<th>( E_g(\text{exp.}) )</th>
<th>( \nu_g )</th>
<th>( V_1 )</th>
<th>( \frac{d}{4\pi g T} )</th>
<th>( E_g(\text{calc.}) )</th>
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<tr>
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<td>0.4</td>
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**TABLE II** Molybdenite.

<table>
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<th>( \nu_g )</th>
<th>( V_1 )</th>
<th>( \frac{d}{4\pi g T} )</th>
<th>( E_g(\text{calc.}) )</th>
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<tr>
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<tr>
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<tr>
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<td>0.8</td>
<td>0.10</td>
<td>18.8</td>
<td></td>
</tr>
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</table>

(1) The value of \( E \) can be calculated by Bethe's theory, as was done by Shinohara in the case of rock salt. However, the convergency of the series, which gives this value, is so slow that the calculation is impossible with the present data of \( F_g \)'s.

Discussions.

The theoretical results agree well with the experiment for graphite, but not for molybdenite. This may indicate that the structure factor for molybdenite adopted in the calculation was not correct. As $v_g$ for large $g$ are considered to be correct even in this case, those for small $g$ can be determined inversely from the experimental values of $(E - E_0)$. Although the carrying out of this procedure is not easy in practice, the estimation showed that both Mo and S atoms are nearly singly ionised in molybdenite crystal. It is interesting that the structure factor can be determined by the procedure such as above, at least in principle, from mere observation of the reflection angle without measuring the intensity.

It is remarkable that the observed value of $E_9$ is considerably smaller than that expected from the general trend of curve $E_n$; the deviation is much larger than the experimental errors. The curve of $E_n$ is not necessarily monotone, especially for crystals which have a parameter as molybdenite, but such a large deviation cannot be explained by varying $f$-values or parameter $u$ in the allowable interval. To account for this fact, $v_8$ must be as large as $v_3$ or $v_4$, but it is unlikely as we see from (5). As the condition of applicability of (3) is satisfied for the ninth order reflection, it is inexplicable on the present theory.

The second anomalous effect of Kikuchi and Nakagawa takes place
only when the surface of crystals is very smooth. It disappears perfectly when the surface is treated. The appearance of the effect may be considered as a criterion of smoothness of the crystal surfaces. This is a surface effect which is not explicable by Bethe’s theory.

In conclusion the author expresses his sincere thanks to Professor S. Nishikawa for his kind guidance throughout this work, and to Dr. T. Yamaguti and Mr. S. Miyake for their valuable criticisms.

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