THE
PHYSICAL REVIEW
A Journal of Experimental and Theoretical Physics Established by E. L. Nichols in 1893
VOL. 59, NO. 9 MAY 1, 1941 SECOND SERIES

X-Ray Diffraction in Random Layer Lattices

B. E. WARREN
George Eastman Laboratory of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received March 7, 1941)

Random layer lattice structures are considered which consist of layers arranged parallel and equidistant, but random in translation parallel to the layer, and rotation about the normal. We call a and b the axes in the layer, and c the axis normal to the layer. In this notation there will be crystalline reflections of type $(00l)$, two-dimensional lattice reflections of type (hk), and no general reflections (hkl). Equations are developed for the intensity distribution in a two-dimensional powder reflection, and for the integrated intensity. Equations are also developed for the particle size in terms of the peak breadth, and for the displacement of the peak. The powder pattern of a heat treated carbon black is presented as an illustration of two-dimensional lattice reflections.

I. INTRODUCTION

THE x-ray diffraction patterns of certain layer type materials indicate that they may exist in a form which is intermediate between the amorphous and the crystalline states. For example, the x-ray patterns of certain heat treated carbon blacks indicate that they are built up from individual graphite layers arranged parallel to one another at about the normal graphite spacing but random in translation parallel to the layer, and rotation about the normal. The powder pattern of such a material consists of two kinds of reflections—crystalline type reflections, and diffuse two-dimensional lattice reflections. The qualitative form of a two-dimensional lattice reflection has been given by von Laue[1] for the limiting case of large two-dimensional gratings. It is the purpose of this paper to develop the general equations for x-ray powder patterns of random layer lattice materials.

[1] M. v. Laue, Zeits. f. Krist. **82**, 127 (1932).

II. DIFFRACTION BY RANDOM LAYER LATTICE BLOCK

The scheme of repetition in each layer is defined by the translation vectors a_1a_2. The separation between layers is given by the vector a_3 perpendicular to a_1 and a_2. The layers are identical and equidistant, but random in translation parallel to the layer and rotation about the normal. It is enough to consider only the random translation since the only reflections allowed on the powder pattern are unaffected by an additional random rotation. The position of atom n in cell m_1m_2, in layer m_3 is given by the vector

$$R_m{}^n = m_1a_1 + m_2a_2 + m_3a_3 + r_n + \delta_{m3}a_1 + \epsilon_{m3}a_2, \quad (1)$$

where r_n is the basis vector for atoms of type n, and δ and ϵ have completely random values. Let us represent the directions of the primary and diffracted beams by unit vectors s_0 and s. The intensity of diffracted radiation in electron

units is then given by

$$I=\sum_{nm} f_n \exp[(2\pi i/\lambda)(s-s_0)\cdot R_m{}^m] \sum_{nm} f_n \exp[-(2\pi i/\lambda)(s-s_0)\cdot R_m{}^n]. \tag{2}$$

Inserting (1) into (2) and summing, we have

$$I=F^2\frac{\sin^2(\pi/\lambda)(s-s_0)\cdot N_1a_1}{\sin^2(\pi/\lambda)(s-s_0)\cdot a_1}\frac{\sin^2(\pi/\lambda)(s-s_0)\cdot N_2a_2}{\sin^2(\pi/\lambda)(s-s_0)\cdot a_2}\sum_{m_3}\exp[(2\pi i/\lambda)(s-s_0)\cdot(m_3a_3+\delta_{m_3}a_1+\epsilon_{m_3}a_2)]\overline{\sum_{m_3}} \tag{3}$$

where N_1a_1 and N_2a_2 are the dimensions of the layer, assumed to be a parallelogram, and F is the structure factor

$$F=\sum_n f_n \exp[(2\pi i/\lambda)(s-s_0)\cdot r_n]. \tag{4}$$

The two sine quotients will be small unless the two Laue equations are approximately satisfied.

$$(s-s_0)\cdot a_1=h\lambda, \quad (s-s_0)\cdot a_2=k\lambda. \tag{5}$$

If h and k are both zero Eq. (3) is independent of the randomness, and assumes the usual form for a crystalline reflection.

$$I_{00l}=F^2\frac{\sin^2(\pi/\lambda)(s-s_0)\cdot N_1a_1}{\sin^2(\pi/\lambda)(s-s_0)\cdot a_1}\frac{\sin^2(\pi/\lambda)(s-s_0)\cdot N_2a_2}{\sin^2(\pi/\lambda)(s-s_0)\cdot a_2}\frac{\sin^2(\pi/\lambda)(s-s_0)\cdot N_3a_3}{\sin^2(\pi/\lambda)(s-s_0)\cdot a_3}. \tag{6}$$

If h and k are not both zero, the phase factors in the summation over m_3 are completely random, the scattering from the individual layers will be incoherent, and the intensity from a single layer will be

$$I_{hk}=F^2\frac{\sin^2(\pi/\lambda)(s-s_0)\cdot N_1a_1}{\sin^2(\pi/\lambda)(s-s_0)\cdot a_1}\frac{\sin^2(\pi/\lambda)(s-s_0)\cdot N_2a_2}{\sin^2(\pi/\lambda)(s-s_0)\cdot a_2}. \tag{7}$$

The diffracted radiation will be of two kinds; crystalline reflections of type $(00l)$, and two-dimensional lattice reflections of type (hk). There will be no reflections of type (hkl). We are interested in the powder pattern of a sample containing a large number of blocks with random orientation. The crystalline peaks of type $(00l)$ are given directly by the usual powdered crystal theory. The next step is to develop the theory of the diffraction pattern of a two-dimensional lattice which takes with equal probability all orientations in space.

III. Powder Pattern of Two-Dimensional Lattice

Since the vector a_3 is perpendicular to a_1 and a_2, the reciprocal vectors b_1 and b_2 will be in the plane of the layer and b_3 will be perpendicular to the layer. The solution of the two Laue equations gives

$$s-s_0=\lambda H+(s-s_0)\cdot a_3b_3 \tag{8}$$

where $H=hb_1+kb_2$.

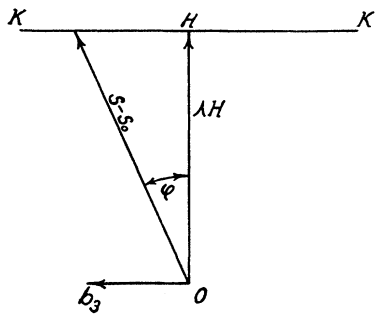

Fig. 1. Reciprocal lattice construction for a two-dimensional lattice.

The significance of Eq. (8) is best seen in the reciprocal lattice construction shown in Fig. 1. The terminal point of the vector $s-s_0$ can lie anywhere on the line KHK passing through the point H and perpendicular to the layer. For a two-dimensional layer the reciprocal lattice becomes a series of parallel lines perpendicular to the layer. Since $|s-s_0|=2\sin\theta$, for each index pair hk there is a minimum value of $\sin\theta$ given by

$$2\sin\theta_0=\lambda H. \tag{9}$$

There will be a continuous distribution of diffracted intensity for all values of $\sin\theta$ greater than $\sin\theta_0$. In the vicinity of θ_0 there will be a concentration in the diffracted intensity since $|s-s_0|$ changes slowly for small values of φ. Each (hk) band will have the form shown in Fig. 4.

In the general case the layers will not be indefinitely large, and there will be an appreciable intensity contribution for the terminal point of $s-s_0$ somewhat off the line KHK. To get the exact intensity distribution in a (hk) reflection, will therefore require the usual integrations involved in the derivation of an integrated intensity. Let P be the power, or total energy per second of diffracted radiation for a particular index pair (hk).

$$P=\int\int IdAdM. \tag{10}$$

P is obtained by integrating the intensity from each layer over the area of the receiving surface, and over dM the number of crystals in each range of orientation with respect to the primary beam. To be able to discuss the shape of a two-dimensional lattice reflection, it is necessary to know the distribution of power with respect to angle. Let us call this quantity $P_{2\theta}$, then P may be expressed by

$$P=\int P_{2\theta}d(2\theta). \tag{11}$$

If we represent any value of $s-s_0$ in terms of a value $(s-s_0)_H$ which exactly satisfies the two Laue equations we have

$$s-s_0=(s-s_0)_H+\Delta s. \tag{12}$$

From (7), the intensity per layer becomes

$$I_{hk}=F^2\frac{\sin^2(\pi/\lambda)\Delta s\cdot N_1a_1}{\sin^2(\pi/\lambda)\Delta s\cdot a_1}\frac{\sin^2(\pi/\lambda)\Delta s\cdot N_2a_2}{\sin^2(\pi/\lambda)\Delta s\cdot a_2}. \tag{13}$$

By restricting our attention to one particular reflection (hk), the usual approximation can be made

$$\frac{\sin^2Nx}{\sin^2x}\rightarrow N^2\exp\left[-\frac{N^2}{\pi}x^2\right]$$

$$I_{hk}=F^2N_1^2N_2^2\exp\{-(\pi/\lambda^2)[(\Delta s\cdot N_1a_1)^2+(\Delta s\cdot N_2a_2)^2]\}. \tag{14}$$

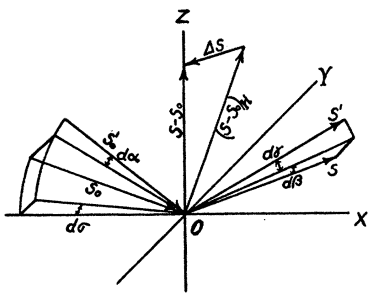

FIG. 2. Displacements of s and s_0 involved in the integration for diffracted power.

We can express Δs in terms of the three variables $p_1p_2p_3$ as follows

$$\Delta s=\frac{p_1}{N_1}b_1+\frac{p_2}{N_2}b_2+p_3b_3, \tag{15}$$

$$I_{hk}=F^2N_1^2N_2^2\exp[-(\pi/\lambda^2)(p_1^2+p_2^2)]. \tag{16}$$

In Fig. 2 let the general vector $(s-s_0)$ be the polar axis. The direction of the primary beam s_0 varies by small azimuth and latitude angles $d\sigma d\alpha$ and the direction of diffracted radiation by the orthogonal displacements $d\beta d\gamma$. The solid angle covered by the primary beam is

$$d\Omega=\cos\theta d\alpha d\sigma \tag{17}$$

and the area of receiving surface covered by the diffracted radiation is

$$dA=R^2d\beta d\gamma. \tag{18}$$

If M is the number of two-dimensional layers in the sample, the number dM for which the primary beam lies within the solid angle $d\Omega$ having the same equivalent orientation as regards a reflection (hk), is given by the proportion

$$dM/mM=d\Omega/4\pi,$$

where m is the two-dimensional multiplicity.

Substituting in (10), we obtain

$$P=\frac{mMR^2}{4\pi}\int\int\int\int I\cos\theta d\sigma d\alpha d\beta d\gamma. \tag{19}$$

By holding σ constant, but allowing small changes $d\alpha$, $d\beta$, $d\gamma$, the vector Δs will receive an increment $d(\Delta s)$ given by

$$d(\Delta s)=(d\alpha-d\gamma)\sin\theta i+d\beta j+(d\alpha+d\gamma)\cos\theta k, \tag{20}$$

where $i\ j\ k$ are unit orthogonal vectors. If we replace the variables α, γ by a new set δ, ϵ at 45° to the former axes, we have

$$\delta=(\alpha+\gamma)/\sqrt{2},\quad \epsilon=(\alpha-\gamma)/\sqrt{2},$$
$$d(\Delta s)=\sqrt{2}\sin\theta d\epsilon i+d\beta j+\sqrt{2}\cos\theta d\delta k. \tag{21}$$

For increments $d\epsilon d\beta d\delta$, the terminal point of Δs sweeps out a volume

$$dV=\sin 2\theta d\epsilon d\beta d\delta. \tag{22}$$

From Eq. (15), for increments $dp_1dp_2dp_3$ we find the terminal point of Δs sweeps out a volume

$$dV=\frac{b_1\cdot b_2\times b_3}{N_1N_2}dp_1dp_2dp_3. \tag{23}$$

Equating the volumes, we have

$$d\epsilon d\beta d\delta=(N_1N_2v_a\sin 2\theta)^{-1}dp_1dp_2dp_3. \tag{24}$$

Substitution in Eq. (19) gives

$$P=\frac{mMR^2}{8\pi N_1N_2v_a}\int\int\int\int\frac{I}{\sin\theta}d\sigma dp_1dp_2dp_3. \tag{25}$$

The integration with respect to $d\sigma$ can be carried out independently. Expressing I in terms of (16), we obtain

$$P=\frac{R^2N_1N_2Mm}{4v_a}\int\int\int\frac{F^2}{\sin\theta}$$
$$\times\exp[-(\pi/\lambda^2)(p_1^2+p_2^2)]dp_1dp_2dp_3. \tag{26}$$

By replacing the variables p_1p_2 by a new set of orthogonal variables v_1v_2 such that v_1 determines the component of Δs parallel to the vector H we obtain

$$P=\frac{R^2N_1N_2Mm}{4v_a}\int\int\int\frac{F^2}{\sin\theta}$$
$$\times\exp[-(\pi/\lambda^2)(v_1^2+v_2^2)]dv_1dv_2dp_3. \tag{27}$$

Let G be a unit vector parallel to H, and set

$$v_1=L(\Delta s\cdot G). \tag{28}$$

The quantity L introduced in (28) has the significance of a particle dimension given by

$$\frac{1}{L}=\left[\left(\frac{b_1\cdot G}{N_1}\right)^2+\left(\frac{b_2\cdot G}{N_2}\right)^2\right]^{\frac{1}{2}}. \tag{29}$$

To get the distribution of power $P_{2\theta}$, the integration is restricted to values of $|s-s_0|$ between r and $r+dr$, where $r=2\sin\theta$. In terms of the cylindrical coordinates used in Fig. 3,

$$dv_1dp_3=Lrd\varphi dr/|b_3|,$$
$$v_1=L(\Delta s\cdot G)=L(r\cos\varphi-\lambda H).$$

Since the exponential factor involving v_2 decreases rapidly we can approximate by replacing the spherical shell by the tangent cylindrical shell and integrating v_2 from $-\infty$ to $+\infty$.

$$P=\frac{N_1N_2R^2mM\lambda}{4A_a}\int\int\frac{F^2}{\sin\theta}$$
$$\times\exp[-(\pi/\lambda^2)L^2(r\cos\varphi-\lambda H)^2]Lrd\varphi dr. \tag{30}$$

For the intense part of a reflection, only small values of φ are of importance, and $\cos\varphi$ can be expanded. By letting

$$a=\frac{\sqrt{\pi L}}{\lambda}(r-\lambda H),\quad x=\varphi(\sqrt{\pi Lr}/2\lambda)^{\frac{1}{2}} \tag{31}$$

$$F(a)=\int_0^\infty\exp[-(x^2-a)^2]dx, \tag{32}$$

Eq. (30) becomes

$$P=\frac{N_1N_2R^2mM\lambda L}{A_a}\int F^2\left(\frac{\lambda}{\sqrt{\pi L}\sin\theta}\right)^{\frac{1}{2}}$$
$$\times F(a)\cos\theta d(2\theta). \tag{33}$$

The power $P_{2\theta}$ is spread over a circle of circumference $2\pi R\sin 2\theta$. Calling $P_{2\theta}'$ the power per unit length of circle, and introducing the intensity of scattering per electron, so that $P_{2\theta}'$ is expressed in absolute units, we have

$$P_{2\theta}'=\frac{P_{2\theta}}{2\pi R\sin 2\theta}\frac{I_0e^4}{m^2c^4R^2}\left(\frac{1+\cos^2 2\theta}{2}\right). \tag{34}$$

TABLE I. *Function F(a).*

a	$F(a)$	a	$F(a)$	a	$F(a)$	a	$F(a)$
−1.2	0.12	−0.4	0.61	0.1	0.96	0.6	1.06
−1.0	0.21	−0.3	0.69	0.2	1.01	0.8	1.04
−0.8	0.32	−0.2	0.77	0.3	1.04	1.0	0.99
−0.6	0.46	−0.1	0.84	0.4	1.06	2.0	0.67
−0.5	0.53	0.0	0.91	0.5	1.07	3.0	0.52

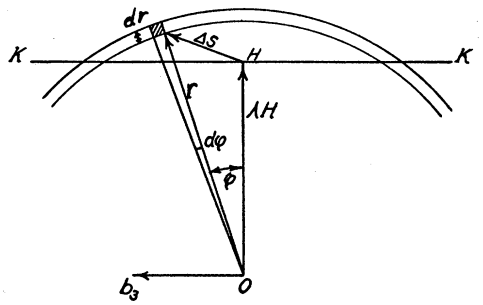

FIG. 3. Cylindrical coordinates used in the integration.

Letting

$$K=\frac{I_0e^4N_1N_2M\lambda^2}{m^2c^4 4\pi RA_a}, \tag{35}$$

we obtain

$$P_{2\theta}'=Km\frac{F^2(1+\cos^2 2\theta)}{2(\sin\theta)^{\frac{3}{2}}}\left(\frac{L}{\sqrt{\pi\lambda}}\right)^{\frac{1}{2}}F(a), \tag{36}$$

where $$a=(2\sqrt{\pi L}/\lambda)(\sin\theta-\sin\theta_0). \tag{37}$$

The function $F(a)$ as defined by Eq. (32) is given in Table I.

For large values of a $(a>3)$

$$F(a)=(\pi/4a)^{\frac{1}{2}}$$

and Eq. (36) reduces to

$$P_{2\theta}'=\frac{KmF^2}{4\sqrt{2}}\frac{(1+\cos^2 2\theta)}{\sin\theta[\sin\theta(\sin\theta-\sin\theta_0)]^{\frac{1}{2}}}. \tag{38}$$

The usefulness of Eq. (38) is restricted by the expansion of $\cos\varphi$ in Eq. (30). For $\sin\theta<1.2\sin\theta_0$ the error in Eq. (38) is less than 5 percent. A more useful equation for large values of a can be obtained from (27). From Fig. 3, we see that if r is appreciably larger than λH, the contribution to the integral for $P_{2\theta}'$ depends only on the length of the reciprocal lattice line KHK intercepted by the two spheres. The integration over v_1 and v_2 can be carried out from $-\infty$ to $+\infty$, and

$$\int dp_3=2\int\frac{dr}{|b_3|\sin\varphi}.$$

Using the relation $\sin\theta_0=\cos\varphi\sin\theta$, and dividing by $2\pi R\sin 2\theta$, and multiplying by the intensity per electron, we find Eq. (26) becomes

$$P_{2\theta}'=\frac{KmF^2(1+\cos^2 2\theta)}{4\sin\theta(\sin^2\theta-\sin^2\theta_0)^{\frac{1}{2}}}. \tag{39}$$

Equation (39) gives in absolute units, the result which has already been derived by von Laue.[1] To plot the distribution of intensity in a two-dimensional reflection Eq. (36) should be used for small values of $\sin\theta-\sin\theta_0$, and Eq. (39) for the larger values. Over small ranges of angle, F^2 can be treated as a constant, otherwise it must be considered as varying continuously with $\sin\theta$, and given by

$$F_{hk}=\sum_n f_n\exp\left[2\pi i\left\{hx+ky+\frac{2a_3z}{\lambda}(\sin^2\theta-\sin^2\theta_0)^{\frac{1}{2}}\right\}\right]. \tag{40}$$

IV. Particle Size from Peak Breadth

The size of a two-dimensional layer in the plane of the layer can be determined from the breadth of the two-dimensional reflection at half-maximum intensity. The dimension L which is determined from a reflection (hk) is the effective dimension of the layer in the direction $H=hb_1+kb_2$. Over the small range of angle included between half-maximum intensity values, the variation in (36) can be considered as due wholly to $F(a)$. From a plot of Table I it is seen that the half-maximum intensity breadth corresponds to a change in a of amount $\Delta a=3.26$. From Eq. (37)

$$3.26=\frac{2\sqrt{\pi L}}{\lambda}\Delta(\sin\theta);\quad L=\frac{1.84\lambda}{B\cos\theta}. \tag{41}$$

It should be pointed out that Eq. (41) for the two-dimensional particle size has exactly the same form as the equation for the crystalline particle size except for a numerical coefficient about twice as large.

V. Displacement of Peaks

The maximum in $F(a)$ comes at $a=0.55$. Calling the position of the maximum θm, we have

$$0.55=(2\sqrt{\pi L}/\lambda)(\sin\theta_m-\sin\theta_0).$$

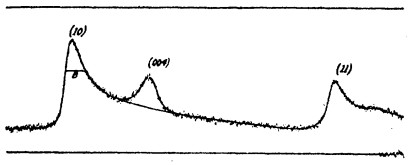

FIG. 4. Microphotometer record of the diffraction pattern of a heat treated carbon black, showing two-dimensional lattice reflections. Radiation Cu $K\alpha=1.539$A, monochromated by reflection from rocksalt.

The maximum is therefore displaced from θ_0 toward larger angles by an amount

$$\Delta(\sin\theta)=0.16\lambda/L.$$

For small particle dimensions L, this displacement of the peak toward larger angles can be quite important. If the two-dimensional character of the reflection were not realized, and the peak were treated as a normal crystalline powder pattern line, erroneous conclusions about lattice contractions could easily be drawn.

VI. Integrated Intensity of a Two-Dimensional Reflection

In order to determine from a powder pattern the amount of material present in the form of independent two-dimensional layers, it is convenient to measure the integrated intensity for a two-dimensional reflection. Although each reflection extends to $2\theta=180°$ it is better to measure only the part extending to a convenient and arbitrary value of $\sin\theta$. We have

$$\text{integrated intensity}=\int_0^{2\theta} P_{2\theta}\,d(2\theta). \quad (43)$$

From Eq. (26) and Fig. 3, we see that if 2θ is taken enough larger than $2\theta_0$, such that the intensity distribution at 2θ is nearly independent of particle size, the contribution will depend only on the length of the reciprocal lattice line KHK within the sphere. Integrating p_1 and p_2 from $-\infty$ to $+\infty$ we find Eq. (26) becomes

$$P=\frac{F^2N_1N_2R^2mM\lambda^2}{4v_a}\int\frac{1}{\sin\theta}dp_3 \quad (44)$$

$$d(\Delta s)=|b_3|\,dp_3=2\sin\theta_0\sec^2\varphi\,d\varphi.$$

By introducing the intensity per electron and dividing by $2\pi R\sin2\theta$, to give the power per unit length of arc, and introducing the abbreviation K from Eq. (35), we obtain

$$P'=Km\int\frac{F^2(1+\cos^2 2\theta)}{2\sin\theta\sin2\theta}\sin\theta_0\sec^2\varphi\,d\varphi. \quad (45)$$

If the range $2\theta-2\theta_0$ is kept small, an average value for F^2 and the polarization factor can be used. Since $\sin\theta_0=\sin\theta\cos\varphi$ Eq. (44) becomes

$$P'=\frac{Km\langle F^2\rangle_{Av}}{2\sin\theta_0}\left\langle\frac{1+\cos^2 2\theta}{2}\right\rangle_{Av}\int_{-\varphi}^{+\varphi}\frac{\cos\varphi\,d\varphi}{(\cos^2\theta_0-\sin^2\varphi)^{\frac{1}{2}}}$$

and the integrated intensity is then given by

$$\int_0^{2\theta}P_{2\theta}'\,d(2\theta)=\frac{Km}{\sin\theta_0}\langle F^2\rangle_{Av}\left\langle\frac{1+\cos^2 2\theta}{2}\right\rangle_{Av}\times\sin^{-1}\left(\frac{[1-\sin^2\theta_0/\sin^2\theta]^{\frac{1}{2}}}{\cos\theta_0}\right). \quad (46)$$

Equation (46) is in a convenient form for evaluation from microphotometer records, and for direct comparison with the integrated intensity of a crystalline reflection.

VII. Example of Two-Dimensional Lattice Reflection

Figure 4 is the microphotometer record of part of an x-ray powder pattern of a heat treated carbon black. In terms of the hexagonal axes of graphite, the reflections appearing are the two-dimensional grating reflections (10) and (11), with the three-dimensional reflection (004) superimposed on (10). The form of a two-dimensional grating reflection is shown very well by the (10) curve,[2] rising very rapidly near θ_0 and then decreasing continuously toward larger angles. From the breadth of the (10) peak at half-maximum intensity the layer dimension in this particular sample is calculated from (41) to be $L=64$A.

[2] The two-dimensional lattice character of certain carbon black reflections has been recognized by a number of investigators. U. Hofmann and D. Wilm, Zeits. f. Electrochemie **42**, 504 (1936); H. Arnfeld, Arkiv f. Mat. Astron. Fys. **B23**, 1 (1932; E. Berl, K. Andress, L. Reinhardt and W. Herbert, Zeits. f. physik. Chemie **A158**, 273 (1932); **A166**, 81 (1933).