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Intensity of Diffraction of Electrons by ZnO

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Electron diffraction patterns of ZnO powder have been obtained in the range from 10 to 80 kv by using two types of camera. The intensity distribution has been determined photographically and shows marked deviations from the intensity distribution of the corresponding x-ray pattern. It has been shown that these deviations are not due to impurities, difference in structure due to methods of preparation, coincidences with another form of ZnO, or due to preferred orientation. The scattering as a function of sin (θ/λ) is discussed on the basis of additional surface reflection, dynamic reflection and refraction of the electrons, and it is found that also these effects cannot account for the anomalous intensity distribution. Complete agreement between experimental and calculated curves for the scattering factor is obtained by assuming a distortion of the electron cloud (M shell of the zinc and L shell of oxygen) resulting in a different parameter for the distance Zn nucleus—oxygen nucleus, and Zn electrons-oxygen electrons. The resulting structure factor has the form

$$S=Z(\mathrm{Zn})-\Sigma F_{n,\,l}(\mathrm{Zn})e^{2\pi i a_{n,\,e} l}+Z(\mathrm{O})e^{2\pi i q l}-F_{n,\,l}(\mathrm{O})e^{2\pi i(q+b_{n,\,e})l}.$$

IT is known that while the scattering of x-rays is not influenced by the nucleus of the scattering atom, electron diffraction is affected by the nucleus as well as by the electronic cloud; electron diffraction is therefore able, at least in principle, to locate the position of both nucleus and electrons in a crystal lattice.

In view of these considerations experimental investigations of the intensity of diffraction of high speed electrons in a powder, using photographic recording, have been undertaken, with the object of determining the atom factor for the diffraction of electrons.[1]

The wave-mechanical theory of the electron diffraction atom factor E, has been put in an especially simple form by Mott,[2]

$$E=(Z-F)/(\sin\theta/\lambda)^2. \qquad (1)$$

θ is the half-angle of scattering, Z the atomic number of the scatterer, and F its x-ray atom factor. This expression is derived for a free atom and is based on the assumption that the atom is spherically symmetric about its nucleus, and that the plane wave of the electron beam is undistorted by the atom. The first of these assumptions, as Mott points out, may not be valid for an atom bound in a crystal lattice, but the second should be acceptable for electrons of sufficiently high velocity.

This expression has been found to agree quite well with experiments carried out on gold, silver and aluminum.[3]

EXPERIMENTAL PROCEDURE

Diffraction photographs were obtained in two cameras illustrated in Figs. 1a and b.

The first camera, Fig. 1a, consists of a brazed and soldered brass box B 25 cm long closed with a lid and rubber gasket. Electrons from a very small conical filament of tungsten, F, are accelerated to the anode by a potential of the order of 20–30 kv, and a fine beam is formed by the slits S_1 and S_2 drilled with 0.15 mm and 0.1 mm holes, respectively. S_3 is a shielding slit on which the specimen is mounted. The diffraction pattern is recorded on a plate (Eastman lantern slide) at P. A two-stage Hg diffusion pump backed by a Cenco Megavac produced a vacuum of 10^{-5} mm Hg. The potential for this camera is supplied by a 30 kv full wave filtered rectifier.

In order to obtain the multiple exposures necessary for establishment of the intensity-density characteristic of the plate, a large diaphragm E with two 30° segments cut away is placed in front of the plate. This diaphragm is rotated about an axis parallel to the beam by a weight (not shown) and stopped in five adjacent positions by a catch operated by a solenoid. The diaphragm is controlled automatically by a motor driven switch which also automatically times the five exposures in the ratio of 1 : 2 : 3 : 4 : 5 by means of a pair of small Helmholtz coils. All the necessary exposures are easily made in

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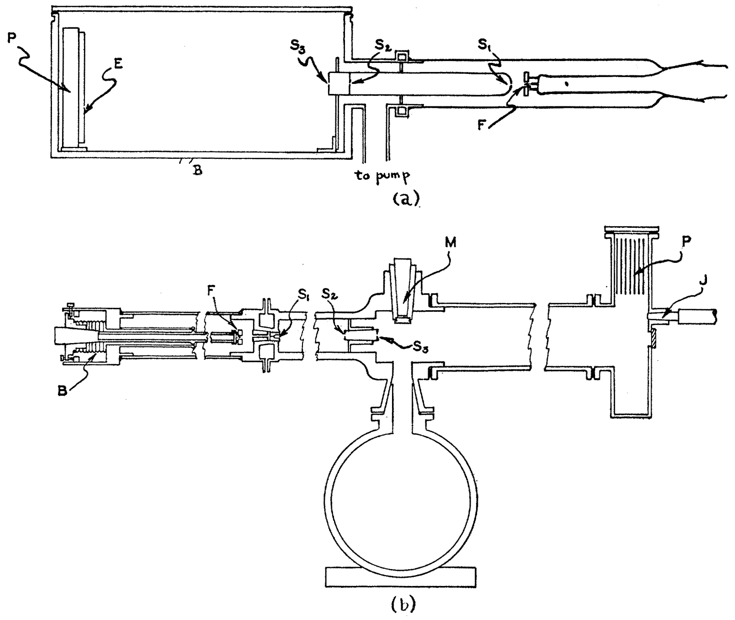
[1] H. J. Yearian and K. Lark-Horovitz, Phys. Rev. **42**, 905 (1932); K. Lark-Horovitz, H. J. Yearian and E. M. Purcell, Phys. Rev. **45**, 123 (1934); K. Lark-Horovitz, H. J. Yearian and J. D. Howe, Phys. Rev. **47**, 331 (1935).

[2] N. F. Mott, Proc. Roy. Soc. **A127**, 658 (1930); G. P. Thomson, Proc. Roy. Soc. **A125**, 352 (1929); H. Mark and R. Wierl, Zeits. f. Physik **60**, 741 (1930).

[3] The apparent discrepancy in the case of Al disappears when a temperature correction is applied. The comparison with the analysis of a number of other substances will be presented in later papers.



(a)

(b)

FIG. 1.

approximately one second more than the total exposure time (of the order of 20 seconds), so that current-voltage conditions are relatively easy to maintain.

The second camera, Fig. 1b, has been used up to 80 kv. It is assembled of brass parts with the removable joints sealed with sulphur free rubber gaskets. Electrons from a small filament *F*, mounted adjustably on a flexible bellows, *B*, form a narrow beam defined by the 0.15 mm hole in the anode S_1, and the 0.10 mm hole in slit S_2. The specimens are mounted either on the shielding slit S_3 or on a universal mounting operated by the double cone joints *M*. The camera is mounted directly on a Holweck molecular pump backed by a Cenco Megavac, giving a very high pumping speed. The potential is supplied by a 120 kv full wave filtered rectifier.

The pattern is recorded on plates held in the magazine *P*. This magazine holds seven plates each of which may be pulled over the camera opening, exposed and returned, by means of a traveling carriage operated by a ground joint *J*. Also a screen with a rectangular opening may be brought into position over the camera so that five exposures may be made in strips on each plate in order to obtain its intensity-density characteristics. The exposures are timed by contacts on a motor-driven screw; these are adjustable to 20 sec. in steps of 1/20 sec.*

Specimens of ZnO were formed by catching the fumes from a zinc arc on the last diaphragm of the slit system. The deposited crystallites grow into the slit opening, and with a sufficiently fine deposit excellent diffraction patterns are obtained, Fig. 2.

The measurements of the rings in this pattern agree very closely with those calculated from x-ray data, as is shown in columns 1 and 2 of Table I. Columns 3 and 4 give a comparison of estimated intensities. It is evident that there are large discrepancies in the intensities which must

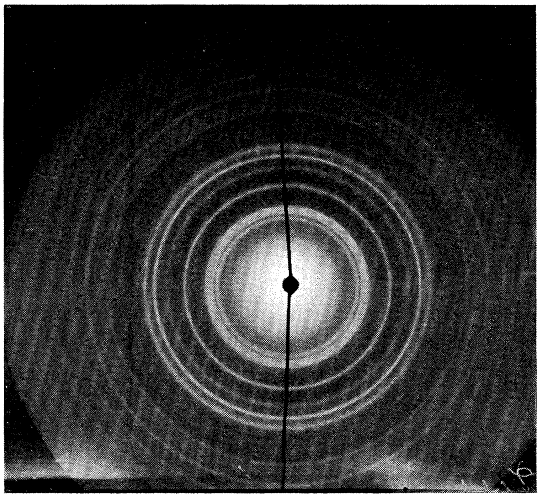


FIG. 2. Pattern of ZnO: 71.5 kv, 1.0 ma, 0.75 sec. exposure.

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* This camera has recently been improved to a quite universal form. A detailed description will be published shortly.

TABLE I.

ZnO Hex. Close packing $a=3.24\text{A}$ $c/a=1.599$ $p=\frac{3}{8}$ C_{6v}^4 Zn(000), $(\frac{1}{3}\ \frac{2}{3}\ \frac{1}{2})$; O(00$p$), $(\frac{1}{3}\ \frac{2}{3}p+\frac{1}{2})$

hkl	sin θ/λ obs.	sin θ/λ calc.	Est. int. elec.	Est. int. x-ray	Mean rel. int.	Ave. dev.	*f*	S_2^2	S_1 Obs. mean
001		.0965						0	
100	.1783	.1782	4	4.5	1.60	.11	6	1	2.14
002	.1941	.1930	6	3.25	2.09	.17	2	4	2.64
101	.2042	.2026	5	5	3.46	.27	12	3	1.87
102	.2637	.2627	5	4	1.46	.10	12	3	4.64
003		.2895						0	
110	.3093	.3086	4	5	1.40	.15	6	4	5.21
111		.3234						0	
103	.3407	.3394	6	4.75	2.97	.32	12	3	8.19
200	.3594	.3563	2	2	.243	.014	6	1	6.74
112	.3654	.3640	4	5	1.48	.15	12	4	6.17
201	.3718	.3692	3	3.5	.528	.065	12	3	4.46
004	.3872	.3860	1	1.75	.236	.018	2	4	7.10
202	.4074	.4053	2	2.25	.266	.054	12	1	7.26
113		.4232						0	
104	.4269	.4252	3	1.25	.197	.040	12	1	7.08
203	.4614	.4592	4	4	.571	.079	12	3	8.91
120	.4752	.4715	1	2.5	.226	.053	12	1	10.5
211	.4835	.4812	2	3.5	.370	.066	24	3	5.89
005		.4826						0	
114	.4973	.4943	2	2.5	.320	.054	12	4	7.13
212	.5165	.5094	5	2.5	.216	.115	24	1	9.26
105		.5144		4	.574	.115	12	3	12.45
204	.5297	.5254	1	1.25	.065	.010	12	1	7.78
300	.5386	.5346	2	3	.271	.036	6	4	11.9
301		.5432						0	
213	.5580	.5533	4	4.75	.524	.105	24	3	10.6
302		.5682	3	3.75	.273	.023	12	4	10.2
115		.5727						0	
006	.5791	.5789	?	1	.041	.011	2	4	10.0
205	.6000	.5999	3	3.75	.277	.024	12	3	12.6
106	.6078	.6059	2		.055	.004	12	1	10.8
303		.6078						0	
214	.6082	.6093	1		.048	.002	24	1	7.39
220		.6173	1	3.5	.080	.024	6	4	10.0
221		.6248						0	
310		.6424			.066	.014	12	1	14.4
222	.6505	.6468			.155	.026	12	4	11.4
311		.6497			.131	.021	24	3	8.63
312	.6586?	.6706			.062	.004	24	1	11.2
215	.6776	.6743			.264	.033	24	3	13.5
007		.6754						0	
206		.6798			.026	.003	12	1	10.6
223		.6741							
107	.7028	.6986							
313	.7099	.7047							
224		.7280							
216	.7466	.7467							

be accounted for. The discrepancy is also apparent in the comparison of electron and x-ray microphotometer records in Fig. 3.

Inspection shows that planes for which the third index is small are relatively too weak in the electron diffraction pattern. For example, in the x-ray pattern 110 is stronger than 103, but this relation is reversed in the electron pattern. It is interesting to note that these same differences are apparent in the electron diffraction patterns of ZnO reproduced by Ponte[4] and Dauvillier[5] and by Finch and Quarrell.[6] According to formula (1) electron intensities should differ from the x-ray intensities, but only as a monotonous function of sin (θ/λ) and not irregularly from peak to peak.

H. Ponte, Comptes rendus **188**, 244 (1929).

[5] M. A. Dauvillier, J. de physique **3**, 229 (1932).

[6] G. I. Finch and A. G. Quarrell, Proc. Roy. Soc. **A141**, 398 (1933).

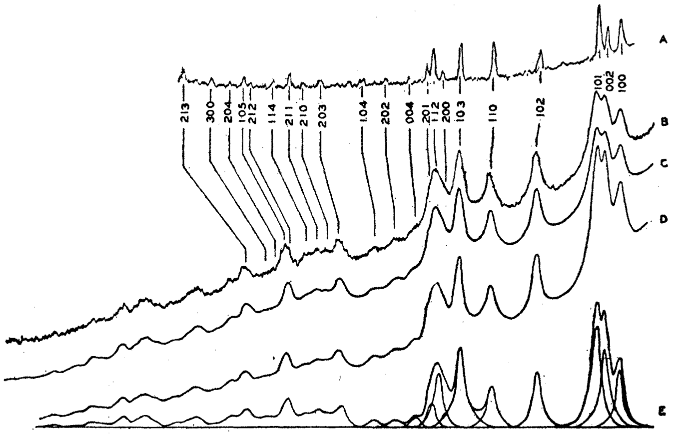

FIG. 3. Microphotometer curves of ZnO diffraction patterns. *A*, x-ray pattern; *B*, electron pattern; *C*, "most probable" trace; *D*, trace *C* converted to optical density; *E*, curve *D* reduced to flat background and partially resolved.

Discussion

Intensity anomalies of this kind might be caused by impurities, preferred orientation, method of depositing powder and influence of its support, or by an erroneous application of the kinematical theory of diffraction neglecting absorption, extinction, refraction and the possible influence of cross gratings. In the search for the possible causes of the unexpected intensity distribution, over 200 plates have been taken under different conditions at potentials ranging from 10 to 80 kv.

No difference has been found between the diffraction patterns from C.P. and spectroscopically pure† zinc. Specimens have been prepared on brass, copper, gold, platinum and molybdenum slits without change. To check the effect of the form of powder deposit, pictures have been taken with both commercial ZnO, and oxide from the arc collected on glass and pressed on the slit. There was no difference in the diffraction patterns from deposits of very large or very small particle size. Zinc oxide from a zinc arc sometimes forms long threads of crystallites. Patterns have been obtained from such single threads, from powder deposited on silk fibers and on thin films of celluloid. All these patterns are identical with the one illustrated.

There is no indication of preferred orientation, but to test for an axis of orientation parallel to the electron beam, a deposit was made on a slit which could be rotated. No change was produced when the slit was rotated in the range from 90° to 30° with respect to the beam. X-ray photographs of one of the specimens, moreover, gave the regular x-ray intensities.

All x-ray data on the structure of ZnO are in agreement with a single space group $C_{6v}{}^4$. A different surface structure, undetectable by x-rays, might affect the electron intensities. A comparison, however, with the intensities of the other possible space groups[7] shows that no combination of these can account for the observed electron intensities.

Coincidence of lines of some contamination could falsify the intensites. An actual impurity is improbable since no extra lines were observed. A comparison of the ZnO pattern with the cubic pattern reported by Bragg and Darbyshire,[8] the pseudomorphic form of the oxide reported by Finch and Quarrell,[6] and with zinc, shows several coincidences but in all cases there are equally strong or stronger lines in these patterns which do not coincide and would be observable if these substances were present.

From these considerations it would seem impossible that the anomalous intensities observed can be due to contamination or to preferred orientation. Further it appears very improbable that they can be explained by absorption or extinction effects. In primary extinction one might expect that intense reflections should be weakened more than weaker ones, but there is no apparent connection between the deviations in the intensities and the expected strength of reflection.

As will be shown in more detail later, the nearer a plane is to being perpendicular to the *c* axis, the more its intensity deviates from normal. To account for this by extinction would require a corresponding regularly increasing degree of imperfection of the crystal for such planes. This seems very artificial. The dynamical theory of electron diffraction developed by Bethe[9] in considering the effects of extinction and interaction of diffracted beam with the incident beam, predicts the appearance of reflections not possible in the usual kinematical theories. Faint "inner rings," discussed below, are sometimes found in the ZnO pattern which might be attributed to such dynamical effects. Their intensities, however, are less than one percent of the stronger regular reflections, and would indicate that the deviations of fifty percent or more observed in the regular pattern are not explainable by dynamical considerations of extinction, etc.

One could possibly explain the dependence of the intensity deviation on the direction of the diffracted rays in the crystal, as being due to absorption. The absorption in crystallites much longer parallel to the *c* axis than perpendicular

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† The pure zinc was obtained from Adam Hilger, London, England.

[7] Wycoff, *The Structure of Crystals*, first edition, p. 275.

[8] W. A. Bragg and J. A. Darbyshire, Trans. Faraday Soc. **28**, 522 (1932).

[9] H. Bethe, Ann. d. Physik **87**, 55 (1928).

to it would weaken reflections from planes parallel to the axis more than it would reflections from planes perpendicular to the axis. Kirchner[10] has found that the total absorption coefficient (scattering plus true absorption) varies, in mica, approximately inversely as the electron velocity. Such a rapid variation of absorption should produce considerably different intensity deviations at different velocities. No noticeable difference in the intensity patterns has, however, been obtained over the whole range from 7 kv to 80 kv, and one must conclude that absorption does not account for the anomalities observed.

There is still the possibility that refraction produces the effect. On a few plates one or more very faint but sharp rings smaller than the first permissible reflection ("fractional orders") have been noted; these usually occurred when the specimen contained large crystallites. These have been explained by K. Lark-Horovitz[11] as a refraction effect since he has shown that although the refraction is negligible when high velocity electrons are incident normally on a diffracting layer and are diffracted from an inner plane, when the diffraction occurs from an exposed surface, refraction is not negligible. Indeed a lattice potential of the order of only 4 volts is necessary to produce a "half order" diffraction from 002 of ZnO.* This effect, however, can hardly be the cause of the anomalous intensity distribution since calculations have shown that the refraction is appreciable only when the incident or diffracted beam, or both, makes a very small angle with the crystal surface, and can practically enter, therefore, only in the case of planes which are developed faces of the crystallites. This necessity of very small angles also requires that the surface be exceedingly flat, "electron optically smooth," and of considerable extent, of the order of 10^3A. From these considerations it is obvious that the whole pattern could hardly be affected by refraction in the way observed. For example, the 100 and 110 intensities are reduced to approximately half as compared with reflections from 001. This would require that at least half the crystallites have these planes developed as large electron optically smooth faces and at the same time have no 001 faces so developed. But in a pseudolayer-lattice like ZnO one would expect the latter type of development to be at least as frequent as the former, and probably much more frequent.** Furthermore, the products of the many necessary refractions should appear either as visible "inner" rings, or as a broadening of the abnormally weak rings on the inner side;† this does not occur. Any broadening observed affects all rings alike without influencing their relative intensities.

The intensities would also be influenced by the diffraction from two-dimensional lattices superimposed upon that from the space grating. The occurrence of cross lattice diffraction has been frequently observed, [12] and has been theoretically treated by v. Laue.[13] Transmission through two-dimensional networks distributed at random results in a ring pattern. This has the appearance of the usual space lattice pattern but because of the variable angles of incidence on the various crystals, these rings, although sharp on their inner boundaries, fall off less rapidly on their outer edges. In this type of diffraction from the hexagonal basal planes of ZnO, the rings formed coincide with the space grating reflections of the type *hk*0, which were shown above to be too weak. Although cross grating reflections from prism planes coincide with some of the observed reflections which are too strong, it is almost certain that the basal plane effect should predominate, so that the observed intensities cannot be explained by cross grating effects. Furthermore, the asymmetry of the lines associated with this type of diffraction is not observed in the pattern.

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[10] F. Kirchner, Ann. d. Physik **13**, 45 (1932).

[11] K. Lark-Horovitz and H. J. Yearian, Phys. Rev. **43**, 276 (1933).

* This explanation of "fractional orders" does not require that they be rational fractions of some plane; they can be any fraction depending upon the lattice potential and the plane spacing. Recently also G. P. Thomson has advanced this explanation (G. P. Thomson, Phil. Mag. **18**, 640 (1934)).

** See for instance the development of zinc crystals, *Handbuch der Physik* (1934), Vol. 24, No. 2, pp. 811–821.

† An effect similar to the one observed by L. H. Germer in another connection. Phys. Rev. **44**, 1012 (1933).

[12] Kikuchi, Jap. J. Phys. **5**, 83 (1928); W. L. Bragg, and F. Kirchner, Nature **127**, 138 (1931); Raether, Zeits. f. Physik **78**, 527 (1932); Steinheil, Zeits. f. Physik **89**, 50 (1934).

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

ATOM FACTOR AND DEVIATION FROM SPHERICAL SYMMETRY

Since none of the possibilities discussed above seemed to explain the observed intensity distribution, an atom factor calculation has been made in order to investigate the atomic scattering in the crystal lattice.

The intensity calculations were made in the following way. Each of the five exposures on a plate was microphotometered on a recording instrument and the optical density of several peaks was computed and plotted against exposure. The resulting density-intensity curves were found to be linear below densities of 0.9 to 1.0. An exposure which nowhere exceeded this limit was then photometered two or three times at different positions. The superposition of these traces gave a "most probable" trace practically free of uncertainties due to grain of the plate. This trace was then converted to optical density by means of an improved design of the "logarithmic protractor" described previously.[14]

After drawing in a background curve, the converted trace was reduced to a flat background and the positions of all peaks marked. The overlapping peaks were then resolved under the condition of consistent summation of ordinates and areas, and their areas taken as a measure of the corresponding intensities. The various steps are indicated in Fig. 3.

ZnO is a hexagonal close packed lattice Zn (000, 1/3 2/3 1/2) and O (00p, 1/3 2/3 1/2+p); $p=0.375$ and $c/a=1.599$.[15] This gives a structure factor which may be written

$$S=[E_Z+E_0e^{2\pi ipl}][1+e^{2\pi i(1/3h+2/3k+1/2l)}]$$
$$=S_1'\times S_2.$$

S_1' is the structure factor of the molecule and S_2 takes into account the two molecules in the basis. By (1), (on the assumption of spherical atom symmetry, etc.)

$$E=\frac{Z-F}{\sin^2\theta/\lambda^2}$$

so that we may define

$$S_1=S_1'\times\sin^2\theta/\lambda^2=(Z_Z-F_Z)+(Z_0-F_0)e^{2\pi ipl}.$$

In terms of the observed intensities

$$I=c\frac{f|S|^2}{\sin^2\theta},$$

where f is the frequency factor, and S_1 can be calculated

$$S_1=C\sin^3\theta\sqrt{I/f|S_2|^2},$$

since S_2 is a purely geometrical term.

The mean intensities of fourteen of the best ZnO plates in the range 18–20 kv are shown in column 6 of Table I.* The mean deviations given indicate a quite high reliability, particularly for the stronger peaks. The experimental values of S_1 deduced from these mean values are shown in column 10 and are plotted against sin (θ/λ) in Fig. 4. In Fig. 5 theoretical F factors for Zn and O are shown and the theoretical values of the scattering functions S_1 calculated from them. Because of the falling-off of the F curves with angle, each $Z-F$ term in S_1 rises with angle and the exponential term produces a separate curve for each value of index l. It is at once obvious how greatly the experimental

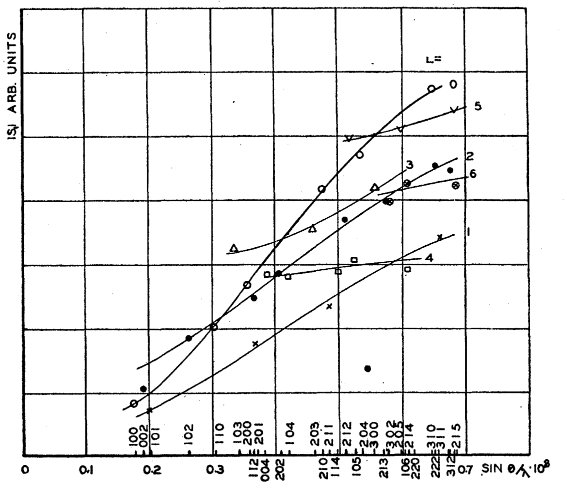

FIG. 4. Observed scattering curves.

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[14] H. J. Yearian, Rev. Sci. Inst. 4, 407 (1933).

[15] Structureberichte, 1913–1918, P. P. Ewald and C. Herman, page 79.

* Calculations have also been carried out for electron velocities up to 80 kv and for temperatures as low as −183 without appreciably different results.

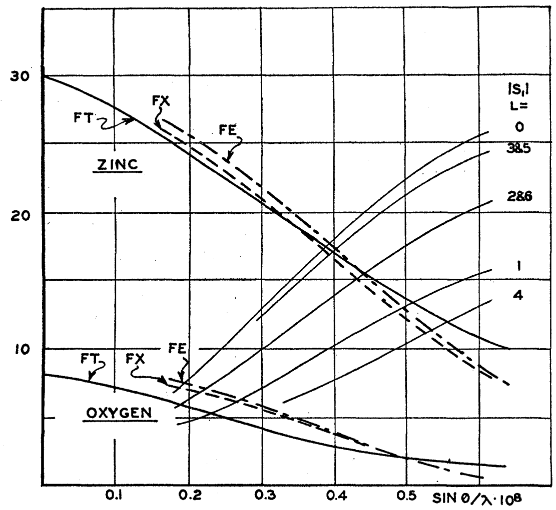

FIG. 5. *F* curves for zinc and oxygen. *FT*, theoretical (Pauling and Sherman); *FX*, experimental x-ray; *FE*, experimental electron. S_1, ideal scattering curves derived from *FT*.

intensities differ from the theoretical. Most of the experimental scattering curves at small angles are much too high; the displacement above the expected position is in general greater the smaller the angle and the larger the value of l.

This behavior gives a hint of possible explanation, for if φ is the angle between a reflecting plane and the c axis, then

$$\sin \varphi = (\lambda/\sin \theta)(l/2c)$$

so that the larger l or the smaller $\sin(\theta/\lambda)$ the more nearly is the plane perpendicular to the c axis, and according to the experimental curves, the higher is its reflecting power above normal. This could be accounted for if the x-ray F curves should be decreased below their normal values at the larger values of φ. This would correspond to atomic electron clouds drawn out from a spherical symmetry into an ellipsoidal form with the major axis in the c direction.

X-ray Debye Sherrer photographs of ZnO analyzed in the same way as the electron diffraction photographs, but using the appropriate x-ray intensity formula, gave scattering curves too consistent among themselves to justify the large deviations in F necessary to fit the observed electron curves under the assumption mentioned above. From these x-ray data the F curves (FX) for Zn and O were found. (The parameter p was evaluated to be $p = 0.378 \pm 0.003$.)† The greater slope of these curves, as compared with the theoretical, (FT), may be caused by anomalous dispersion, since Cu K radiation was used. An absorption correction after the method of Rusterholz[16] or Blake[17] would result in still steeper curves. These differences in slope are quite consistent with a temperature correction of the form $e^{-B \sin^2 \theta/\lambda^2}$. If the Debye-Waller exponent is used as a rough approximation for the correction in a composite hexagonal crystal, the data are satisfied by a characteristic temperature of $\theta = 355°$.

Another explanation of the rise of the observed electron scattering curves with increasing angle φ between c axis and reflecting plane, is suggested by the fact that the electron and nuclear scattering is out of phase. If the center of the electron clouds is not quite coincident with the nucleus but is displaced slightly along the c axis, then an additional phase shift will enter in the structure factor and this will increase the resultant amplitude. This increase would be greatest for large values of l and for F values comparable with Z, i.e., at small values of $\sin(\theta/\lambda)$. This possibility seems reasonable also from considerations of the ZnO structure. In an ideal hexagonal close packed lattice with axial ratio $c/a = 1.633$ and parameter $p = 3/8 = 0.375$, each atom is at the center of gravity of a tetrahedron formed by atoms of the opposite kind. In the actual ZnO lattice these relations are disturbed. The axial ratio is $c/a = 1.599$ and $p = 0.375$. With these values the Zn−O distance along c and the altitudes of the tetrahedrons in this direction are decreased about two percent. The distance from a Zn atom to O atom along c is 1.94A, but to its three other O neighbors the distance is 2.041A, a difference of 5 percent. The angles between Zn−O bonds are also considerably affected. To maintain equilibrium with these changes, a slight shift of the electron center away from the nucleus might very well arise.

A first approximation to the effect of such a shift was obtained in the following way. Since

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† Precision measurements are now being carried out by K. Lark-Horovitz and collaborators.

[16] Rusterholz, Helv. Phys. Acta. **4**, 68 (1931).

[17] F. C. Blake, Rev. Mod. Phys. **5**, 169 (1933).

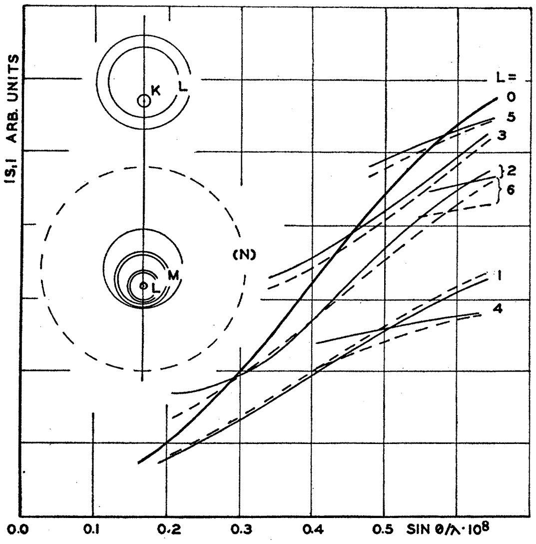

FIG. 6. Calculated scattering curves. Model of ZnO molecule with electron shells displaced to produce dotted curves; (scattering effect of zinc N shell negligible).

the scattering curves for $l=0$ and $l=1$ would be least affected by any dissymmetry along the c axis, these two experimental curves of Fig. 4 were used to calculate the experimental F curves (FE) shown in Fig. 5. Assuming the parameter p for the distance between zinc and oxygen electron centers, q for that between zinc and oxygen nuclei, and a for that between the zinc nucleus and electron center, the structure factor S_l becomes

$$S_l = Z_{\text{Zn}} - F_{\text{Zn}} e^{2\pi i a l} + Z_{\text{O}} e^{2\pi i q l} - F_{\text{O}} e^{2\pi i (p+a) l}.$$

With the experimental F values and assumed values of p, q and a, this complex summation was carried out. All combinations within the range $0.37 < p < 0.39$; $0.36 < q < 0.43$; $-0.05 < a < +0.05$ were tried. The only combination which gave curves approaching the experimental ones was with $p=0.38$, $q=0.37$, and $a=-0.015$.

In these trials it was soon found that a very satisfactory set of curves could be constructed if it were allowed to let parameter a increase with angle φ. This would correspond to saying that the effective electron diffracting center of the atom, as approximated by a spherical distribution, moves farther from the nucleus for planes approaching perpendicularity with the c axis. This would seem to be at least possible for an electron distribution somewhat pear shaped in form. The best set of curves obtained under this assumption, with $p=q=0.38$, $a=+0.01$, for $\varphi < 55°$ and $a=+0.02$ for φ greater than 55°, is shown as full lines, in Fig. 6. Comparison with the observed curves, Fig. 4, shows a rather remarkable agreement.

The satisfactory nature of this agreement was thought to warrant an attempt to justify the rather arbitrary assumption made of a variable nucleus-electron parameter. Since there is at present no theoretical basis for a rigorous calculation of F factor for a nonspherical electron distribution, an approximation was made by assuming each electron shell displaced a slight but fixed distance along the c axis, each shell remaining spherical.

Using F factors of the various shells from the data of Pauling and Sherman,[18] computations show that satisfactory scattering curves are obtainable with only the M shells displaced. From Bohr-Coster diagrams and the size-screening constants of Pauling and Sherman, the energies and average radii of the 3,0; 3,1 and 3,2 sub-shells of zinc are approximately: $E=136$, 90 and 12 volts per electron; and $R=0.25$, 0.28 and 0.39A, respectively. Keeping the relative displacements of the shells in rough conformation with these data, curves were constructed for various displacements. Denoting the displacements of the electron shells of zinc and oxygen by a_{nl} and b_{nl}, respectively; the set of values, $a_1=a_2=b_1=0$; $a_{3,0}=a_{3,1}=0.01$; $a_{3,2}=0.04=b_2$ corresponding to the model shown gave the dotted curves in Fig. 6. Thus distortion of the M shells alone,* if sufficiently great, may account for the observed intensities.

The rather large changes produced by these displacements are, of course, due to the 180° phase difference which exists between the nuclear and electronic scattering. At small angles where F approaches Z, an additional small phase shift in the summation has a large effect in the sum. These electronic displacements have little effect on the x-ray intensities. X-ray scattering curves computed with the same parameter values do not deviate by more than 5 percent from those calculated without displacements.

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[18] L. Pauling and J. Sherman, Zeits. f. Krist. **81**, 1 (1932).

* We are indebted to Dr. Guido Beck for a valuable discussion of this point.

It has been suggested that calculation of the scattering produced by atoms slightly extended from the spherical form along the tetrahedral bond direction, as would be consistent with the peculiar tetrahedral binding in ZnO, might lead to curves in agreement with the experiments.* Rough calculations of the effect of displacing part of the zinc and oxygen scattering power along the four bond directions, instead of along only the *c* axis as formerly, have been made by the writer. Although such considerations are probably poor approximations of the actual tetrahedral effect, it seems quite conclusive that as long as the scattering centers are equivalent and displaced equally, the general features of the observed curves cannot be reproduced. A dissymmetry among the four directions approximately equivalent to those found in the earlier trials seems to be essential.

Considerations of the possible explanations of the anomalous intensities present in all electron diffraction photographs of zinc oxide, lead to the conclusion that distortions of the atomic electron clouds, which are plausible in principle, must be assumed. The degree of distortion necessary for explanation of the experiments is greater** than would be expected, unless the detailed quantum-mechanical investigation of electron distribution gives an unexpectedly large dissymmetry.

Effects similar to those observed in ZnO are apparently present in the diffraction from BeO, which is of the same crystal type, although sufficiently good photographs for a trustworthy analysis have not yet been obtained. Indications of the effect have been found in diffraction from ZnS and probably also exists in the case of MoS_2 as noted by K. Lark-Horovitz.

My thanks are due Professor K. Lark-Horovitz for the suggestion of this problem, and for his constant aid throughout its course. My thanks are also due Mr. A. I. May and Mr. W. C. Holden, of the Physics Shop, for the great care with which they have carried out the design of the apparatus used in the investigation.

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* We are indebted to Dr. H. A. Bethe for a discussion of this possibility. Theoretical calculation of the electron distribution in tetrahedral binding is now in progress in these laboratories under the direction of Dr. L. Nordheim.

** This has been pointed out to us in discussion by Dr. G. Beck.

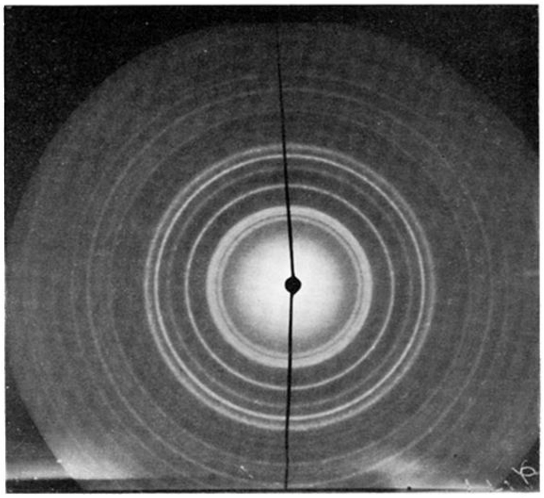

Fig. 2. Pattern of ZnO: 71.5 kv, 1.0 ma, 0.75 sec. exposure.