APRIL 1, 1940 PHYSICAL REVIEW VOLUME 57

Intensity Distribution in X-Ray and Electron Diffraction Patterns

X-Ray Atom Factors of Zinc in Zinc Oxide and Chemical Binding*

C. H. EHRHARDT** AND K. LARK-HOROVITZ
Purdue University, Lafayette, Indiana

(Received November 15, 1939)

Electron diffraction patterns of zinc oxide show intensities markedly deviating from the ones calculated under the assumption of a spherically symmetrical electron distribution in the atom. Possible explanations were suggested on the basis of a shift of the electron cloud with respect to the nucleus, a distortion of the crystal lattice, a distortion of the electron cloud, and particularly of the valence electrons, or effects of dynamical reflection of the electron waves not taken into account in the kinematic theory. For a final decision between these possibilities, x-ray diffraction patterns from a flat sample of zinc oxide have been obtained photographically, with monochromatic Cu $K\alpha$ radiation, and the relative intensities measured. From these results it is possible to calculate the x-ray atom factors for zinc, and thus to construct theoretical electron diffraction curves. These reproduce the essential features of the electron diffraction experiments of K. Lark-Horovitz and H. J. Yearian. Therefore, the observed intensity anomaly must be due to anomalous F factors in the expression for electron diffraction intensity $(Z-F)^2[(\sin\theta)/\lambda]^{-4}$ rather than to effects of dynamical reflection neglected in the kinematic theory. This is also in agreement with the explanation by James and Johnson since the x-ray intensities of our experiments are in better agreement with the theoretical values obtained by using the distorted charge distribution as calculated by James and Johnson, than they are with values based upon the symmetrical distribution of Pauling and Sherman. Discrepancies at larger values of $(\sin\theta)/\lambda$ are discussed in connection with temperature and order-disorder effects: the combination of electron diffraction and x-ray patterns allows one to distinguish between intensity anomalies due to distortion of the electron cloud and effects due to some other factors such as order-disorder.

1. X-RAY AND ELECTRON ATOM FACTORS

It is possible to determine atom factors not only from x-ray, but also from electron diffraction patterns. The intensity distribution in an electron diffraction pattern is much more sensitive to changes in the F factor than it is in an x-ray pattern. In the case of electron diffraction the intensity is determined by the quantity $(Z-F)$ where Z is the atomic number of the scattering atom. For small values of $(\sin\theta)/\lambda$, F is of the order of Z, and small changes in F can therefore produce comparatively large changes in $Z-F$ and, accordingly, in the intensity distribution of the diffraction pattern. Investigations of electron diffraction patterns of zinc oxide,[1, 2] have shown that the intensity distribution differs markedly from the intensity distribution of the corresponding x-ray pattern and from the intensities calculated under the assumption of spherical distributions of electrons around the zinc and oxygen nuclei. It was shown that this intensity anomaly cannot be due to trivial experimental factors such as impurities, preferred orientation, or crystal growth nor to a distortion of the crystal lattice,[3] but must be due either to an intrinsic change in the F factor resulting from distortion of the electron cloud[4] by the crystal bonds, or to some dynamic effect unaccounted for in the kinematical theory of electron diffraction. Since the lines predicted by the dynamical theory, but forbidden by the ordinary structure factor, have only been found occasionally and with extremely small intensity, the first alternative seemed preferable.

Since the *apparent* intensity distribution in the x-ray pattern, when estimated visually, agrees with that expected for the accepted structure, (Wurtzite) the problem was to explain the intensity anomaly of the electron diffraction pattern without changing the qualitative character of the predicted intensity distribution of

---

* Presented at the Washington meeting of the American Physical Society, December, 1938, Phys. Rev. **55**, 605 (1939). Submitted as a thesis to the Faculty of Purdue University by C. H. Ehrhardt.

** Now with Universal Oil Products Company, Riverside, Illinois.

[1] H. J. Yearian and K. Lark-Horovitz, Phys. Rev. **42**, 905 (1932).

[2] H. J. Yearian, Phys. Rev. **48**, 631 (1935).

[3] V. A. Johnson and L. W. Nordheim, Phys. Rev. **51**, 1002 (1937).

[4] V. A. Johnson and H. M. James, Phys. Rev. **53**, 327 (1938); H. M. James and V. A. Johnson, Phys. Rev. **56**, 119 (1939); V. A. Johnson, this issue.

the x-ray pattern. It seems possible to explain the main intensity anomalies without violating the qualitative x-ray data by assuming a model in which the zinc and oxygen atoms are linked together along the c axis in a similar way as are the atoms in a diatomic molecule; that is, by assuming that two of the valence electrons are smeared out over an ellipsoid along the c axis.[4]

To decide definitely whether this explanation is correct or whether the dynamic theory must be taken into account, it is necessary to find the x-ray atom factor for zinc in zinc oxide. This would allow direct comparison with the theoretical considerations, and should also make it possible to construct electron diffraction intensities from the experimental x-ray atom factors.

2. Experimental Problem

For this purpose it is necessary to measure the scattered intensities, eliminate geometric and pure structural factors common to both electron diffraction and x-ray patterns, and finally to compare the x-ray atom factor obtained: (a) with the calculated values, and (b) with the observed intensities in the electron diffraction pattern.

The experimental procedure consists, therefore, of the following steps: (a) Photographic registration of diffraction patterns with exposure chosen for different intensity regions such that the photometric density, $D\leqq 1$; (b) Construction of the most probable photometer curve from the diffraction pattern; (c) Reduction of this curve to density; (d) Correction for absorption; (e) Reduction to relative atom factors by eliminating the structure factor and correcting for temperature motion.

For comparison with the electron diffraction pattern, it is only necessary to determine relative values of the atom factors. These can be computed from the observed relative intensity. We can write for the intensity I:

$$I=KH|S|^2 f(\theta)T,$$

where K is a constant containing experimental factors due to the geometry of the arrangement; H is a frequency factor for the different planes; S is the crystal structure factor, $\Sigma_n F_n \exp\left[2\pi i(hx_n+ky_n+lz_n)\right]$; hkl are the Miller indices of the reflecting plane; xyz are the coordinates of the nth atom in the unit cell; $F(n)$ is the quantity in which we are primarily interested: the atom factor; $f(\theta)$ is a pure function of angle and contains the polarization factor and the Lorentz factor; θ is the Bragg angle for reflection; T is the temperature factor (see later).

3. Experimental Procedure

(a) X-ray source and camera

As a source of CuKα x-rays, a demountable tube[5] was used in connection with a rocksalt monochromator. Exposures of 8 to 60 hours were made in a cylindrical camera of 270 mm circumference. The camera could be rotated about its own axis, and was mounted on a brass plate pivoted on the axis of the monochromator so that proper adjustment could be easily made. For simplicity of absorption correction, a flat sample was used of such thickness that the incident beam was completely absorbed.

As a check on previous work on the geometrical structure, the diffraction pattern of a sample of ZnO paste on a silk thread was investigated. The spacings found were in agreement with those of previous investigations.[6]

(b) Photographic density determination

The pattern used for intensity measurements were recorded on a microphotometer of the Moll type. To eliminate possible effects of grain in the film a number of microphotometer traces were superimposed and a most probable trace constructed. This trace (Fig. 1) was then converted into optical density with the logarithmic protractor.[7] By using only those portions of the film for which the density was directly proportional to the incident x-ray intensity ($D\leqq 1.0$), the area of the peaks on the density trace could be taken as a measure of the intensity. In order to cover the complete diffraction pattern so that the strong peaks would not lie outside the range of unit density and still get an appreciable density for weaker reflections, overlapping exposures were used. In this procedure, a film was taken

---

[5] E. P. Miller, Rev. Sci. Inst. **4**, 379 (1933).

[6] W. L. Bragg, Phil. Mag. **39**, 647 (1920); L. Weber, Zeits. f. Krist. **57**, 398 (1922); G. Aminoff, Zeits. f. Krist. **57**, 204 (1922).

[7] An improved form of the instrument described by Yearian, H. J. Yearian, Rev. Sci. Inst. **4**, 407 (1933).

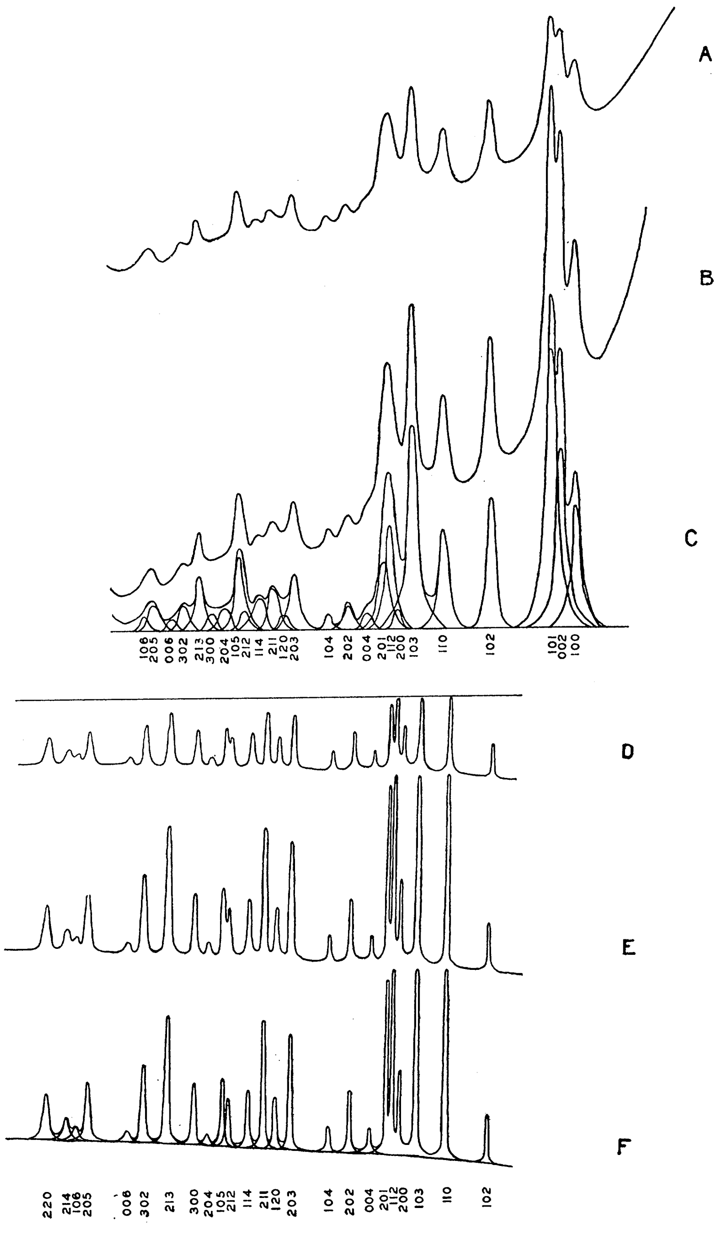

FIG. 1. Electron diffraction and x-ray photometer traces. A. Electron diffraction photometer trace; B. Curve *A* reduced to density; C. Curve *B* reduced to flat background and resolved; D. X-ray photometer trace (reduced by $\frac{1}{3}$ relative to *A*); E. Curve *D* reduced to density; F. Curve *E* resolved.

such that the strongest peak did not exceed unit density, and the ratio of its intensity to other weaker peaks was determined. A second picture was then taken in which the strongest peak was highly over-exposed, but in which the weaker peaks of the first picture were brought up nearly to unit density. The ratio of their intensities to those of still weaker peaks was determined, thus giving, indirectly, the ratio of intensities with respect to the strongest lines.

4. Corrections

(a) Absorption correction

Before any interpretation of the intensities can be made, several corrections have to be applied. For a flat sample of infinite thickness, the absorption correction is given by the expression:

$$I=[1-\cos\beta/\cos(\phi+\beta)]^{-1},$$

where ϕ is the angle between the scattered beam and incident beam and β is the angle between the incident beam and the normal to the sample. Choosing the value at the point $\phi=\pi-\beta$ as unity, the relative absorption correction for all other angles can be evaluated. The measured areas were multiplied by the appropriate absorption correction to give the corrected relative intensities.

(b) The temperature correction

The atom factor F_T for an atom bound in a crystal at a temperature T is related to the atom factor for a free atom F_0 by the relation

$$F_T=F_0\cdot e^{-M},$$

where M is a function of Θ/T and $\sin^2\theta/\lambda^2$, Θ being the characteristic temperature of the crystal. The form of the temperature correction depends on whether the crystal is isotropic or anisotropic and whether it contains only one type of atom or different atoms. The temperature correction is well known theoretically for the case of isotropic crystals[8] and for certain cases of anisotropic crystals[9] (Zn,[10] Cd,[11] and others). The anisotropy is most important for crystals strongly deviating from complete symmetry,[12] but, since zinc oxide has an axial ratio of 1.599 as compared to the ideal ratio 1.633, a simple temperature correction has been used. However, the fact that the crystal is somewhat distorted, and that it contains two types of atoms, makes the application of this simple correction an approximate one. We have used as a characteristic temperature 355°K, a value used success-

---

[8] P. Debye, Ann. d. Physik **43**, 49 (1914); I. Waller, Ann. d. Physik **83**, 154 (1927).

[9] C. Zener, Phys. Rev. **49**, 122 (1936).

[10] E. O. Wollan and G. G. Harvey, Phys. Rev. **51**, 1054 (1937).

[11] G. W. Brindley, Proc. Lond. Phil. Soc. **3**, 200 (1936).

[12] G. W. Brindley and P. Ridley, Proc. Phys. Soc. Lond. **50**, 751 (1938).

TABLE I. *Calculation of molecular structure factor S_1^0 from observed intensities.*

hkl	$\frac{\sin\theta}{\lambda}$	Mean observed intensity	Absorption correction	Corrected intensity	H	$\lvert S_2\rvert^2$	$f(\theta)$	obs. S_1t	e^{-M}	S_1^0
$\beta=75°$										
100	0.178	1335	1.505	2010	6	1	20.96	4.00	0.982	4.07
002	.193	895	1.412	1263	2	4	17.74	2.98	.978	3.05
101	.203	2045	1.357	2760	12	3	15.85	2.21	.977	2.26
102	.263	600	1.175	705	12	1	8.901	2.56	.960	2.77
110	.309	1114	1.103	1231	6	4	6.13	2.89	.940	3.08
103	.340	945	1.071	947	12	3	4.925	2.31	.93	2.48
$\beta=60°$										
200	0.357	385	1.235	476	6	1	4.42	4.23	0.92	4.6
112	.364	1480	1.204	1785	12	4	4.19	2.97	.92	3.23
201	.370	900	1.177	1058	12	3	4.09	2.67	.915	2.93
004	.386	184	1.155	213	2	4	3.74	2.65	.906	2.93
202	.406	396	1.107	438	12	1	3.37	3.29	.900	3.76
104	.425	141	1.092	154	12	1	3.13	2.03	.890	2.28
203	.460	705	1.052	742	12	3	2.83	2.67	.870	3.07
120	.472	267	1.041	278	12	1	2.76	2.89	.862	3.35
211	.482	780	1.033	807	24	3	2.74	2.02	.858	2.35
114	.494	460	1.028	473	12	4	2.71	1.91	.850	2.24
212	.510	359	1.021	367	24	1	2.72	2.37	.840	2.82
203	.514	515	1.013	523	12	3	2.73	2.31	.837	2.76
204	.525	141	1.008	142	12	1	2.77	2.07	.830	2.49
300	.535	450	1.004	452	6	4	2.84	2.57	.825	3.12
213	.553	1126	1.001	1127	24	3	3.02	2.27	.813	2.79
302	.569	603	1.000	603	12	4	3.25	1.96	.805	2.44
006	.579	95	1.002	95	2	4	3.50	1.84	.796	2.31
205	.599	544	1.010	550	12	3	4.13	1.92	.785	2.42
106	.605	128	1.015	130	12	1	4.40	1.57	.782	2.00
214	.609	210	1.019	214	24	1	4.62	1.39	.78	1.78
220	.617	402	1.030	415	6	4	5.23	1.82	.775	2.34

fully before[2] and we have therefore, $M=0.68\times10^{-16}\sin^2\theta/\lambda^2$. Recent experimental investigations of the temperature correction by electron diffraction[13] indicate that our assumption is justified, and the temperature function can be well approximated by a monotonic function using $\Theta=355°\text{K}$.

(c) Correction for anomalous dispersion

Since Cu $K\alpha$ radiation has been used it is necessary to take into account the correction in atom factor for anomalous dispersion due to the K-absorption edge of the zinc atom. This atom factor defect can be calculated theoretically[14] from the theory of anomalous dispersion of x-rays as $\Delta F=F_0-F$, and it is found, in our case, that $\Delta F=2.15$. Since there is no apparent variation of ΔF with $\sin\theta$, it is possible, for comparison of the experimental values with the theoretical values, to subtract the atom factor defect from the theoretical values.

5. STRUCTURE FACTOR

Zinc oxide crystallizes in a hexagonal structure of the Wurtzite type, consisting of a hexagonal close-packed lattice of Zn, and another of O displaced a distance u along the c axis. The coordinates of the Zn atoms are (000), (1/3, 2/3, 1/2), and the coordinates of the oxygen are $(00u)$ and $(1/3, 2/3, 1/2+u)$. The axial ratio is $c/a=1.599$ with $c=5.18$, $a=3.24$ (as compared with an ideal ratio $2(2/3)^{\frac{1}{2}}=1.633$). Former x-ray investigations of ZnO have led to the assumption of a value for the parameter $u=3/8$, since this value leads to no apparent conflict with the observed intensities. Parameter values between 0.36 and 0.39 lead to only small changes in the intensities which cannot be determined from powder photographs alone, since the intensity anomalies must also be considered. For the purpose of this investigation the parameter value was therefore assumed to be 3/8. With this value, the distance Zn—O along the c axis is 1.94A and the distance to the three other oxygens surrounding the Zn atoms is 2.04A. The lattice, therefore, deviates somewhat from the ideal structure.

TABLE II. *Comparison of experimental values of S_1^0 with theoretical values.*

hkl	$\frac{\sin\theta}{\lambda}$	EXPT. NORMALIZED	AVERAGE DEVIATION	*P–S* SPHERICAL DISTRIBUTION	*J* AND *J* 3 VALENCE ELECTRONS	*J* AND *J* 2 VALENCE ELECTRONS
100	0.178	30.3	0.4	29.2	32	31.1
110	.309	23.7	.3	22.3	24.8	23.9
200	.359	20.2	.5	19.8	22.1	21.3
120	.472	15.3	.5	14.5	16.3	15.7
300	.535	13.4	.5	12.2	13.7	13.2
220	.607	10.5	.4	10.1	11.2	10.9
101	.203	17.8	.04	18.5	19.4	19.1
201	.369	12.1	.6	14	14.6	14.2
211	.481	10.1	.25	10.4	11.0	10.8
002	.193	22.8	.4	23.2	24	23.7
102	.263	20.6	.3	20.4	20.9	20.8
112	.364	13.6	.12	16.6	17.1	16.8
202	.405	14.3	1.0	14.9	15.3	15.2
212	.509	11.7	.3	11	11.2	11.1
302	.568	10.4	.04	9.5	9.7	9.6
103	.339	19	.05	19.9	18.9	19.2
203	.459	13.3	.2	14.5	13.6	13.9
213	.553	11.5	.2	11.1	10.1	10.9
004	.386	12.4	.2	12.4	12.2	12.2
104	.425	10	.3	11.2	11	11
114	.494	9.5	.2	9.3	9.1	9.2
204	.525	10.2	.7	8.5	8.3	8.4
214	.609	7.3	.45	6.7	6.5	6.6
105	.514	11.7	.4	12.3	12.6	12.5
205	.600	10.1	.3	10.1	10.5	10.4
006	.579	9.9	.7	9.3	9.6	9.5
106	.606	8.0	.45	8.7	9	8.9

The structure factor for ZnO is given by

$$S=(F_{\text{Zn}}+F_{\text{O}}e^{2\pi iul})[1+\exp(2\pi)i(1/3h+2/3k+1/2l)]=S_1\times S_2.$$

S_1 (a function of $\sin\theta/\lambda$ and l) is the structure factor of the ZnO molecule and S_2 takes into account the two molecules in the unit cell. From the observed intensities I we can calculate relative values of S_1 from*

$$S_1=\left(\frac{I}{KH|S_2|^2f(\theta)}\right)^{\frac{1}{2}},$$

where the symbols have the meaning defined above.

Out of the total of about 50 pictures the average results of the best nine have been evaluated

---

[13] R. M. Whitmer and H. J. Yearian, Phys. Rev. **55**, 1114 (1939).

[14] H. Hönl, Ann. d. Physik **16**, 625 (1933).

* Since we have used a monochromater the polarization factor is not the simple factor $\frac{1}{2}(1+\cos^2 2\theta)$ but is given by $\frac{1}{2}(1+\cos^2 2x\cos^2 2\theta)$ where $\cos^2 2x$ for CuK and NaCl(100) is equal to 0.724

$$f(\theta)=\frac{1+0.724\cos^2 2\theta}{\sin^2\theta\cos\theta}.$$

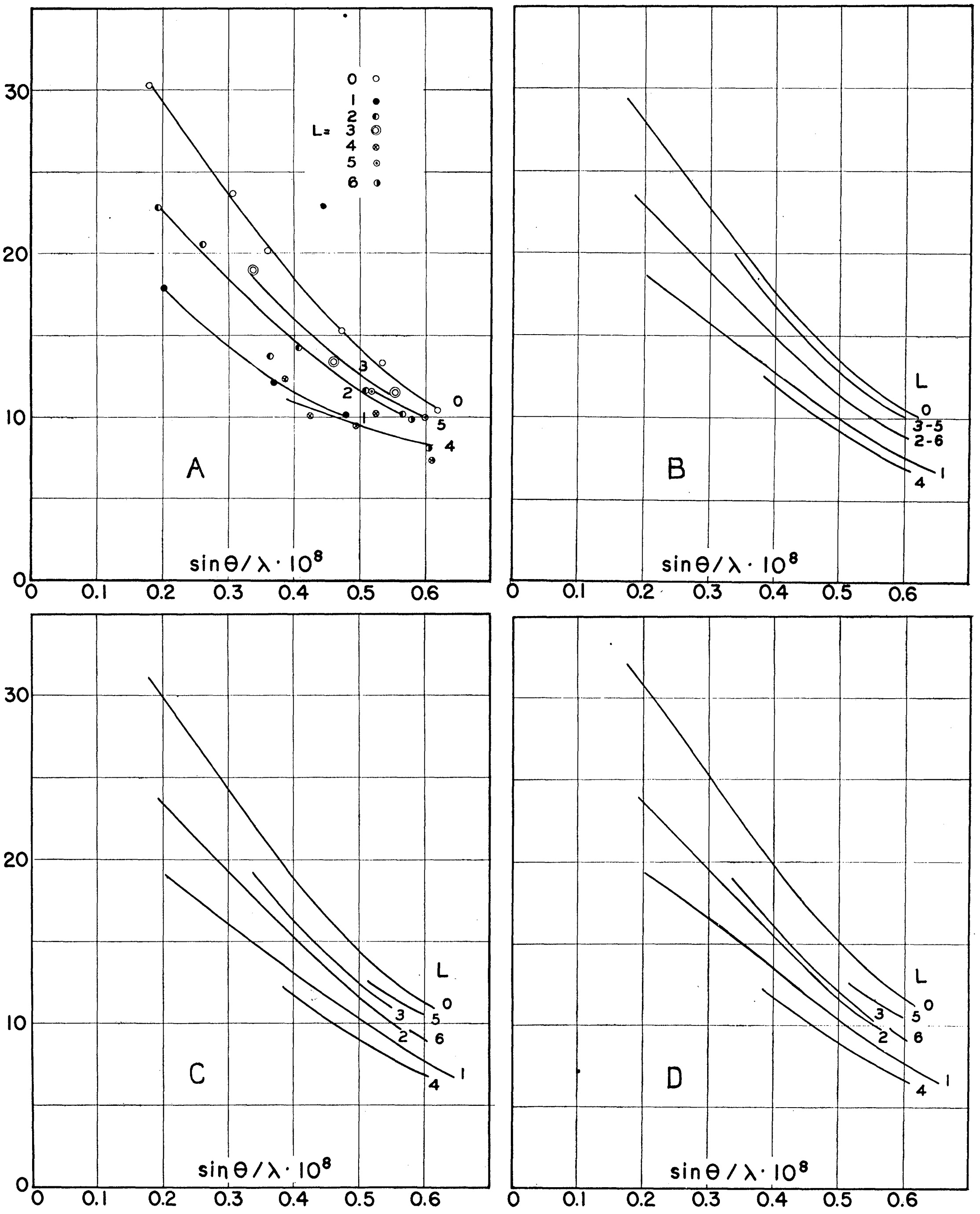

FIG. 2. X-ray structure factor S_1^0 for the zinc oxide molecule. A. Experimental curves; B. Theoretical curves based on spherically symmetric electron distribution (Pauling-Sherman); C. Theoretical curve based on ellipsoidal distribution of 2 of the valence electrons (James and Johnson); D. Theoretical curve based on ellipsoidal distribution of 3 of the valence electrons (James and Johnson). *Note:* L in the figure has the same significance as l in the text.

and the results are shown in Table I. The last column of Table I gives S_1^0, the observed structure factor for the ZnO molecule corrected for temperature.

6. ATOM FACTORS EVALUATED FROM S_1^0

(a) X-ray F factors for ZnO

The values obtained for S_1^0 can now be used for comparison with the theoretical calculations and the experimental electron diffraction curves. This is more satisfactory than complete reduction to individual atom factors, which is a rather difficult, and not always unique, procedure.

For this purpose the experimental values were normalized to the theoretical values, computed with a spherical electron distribution function and a parameter $u=3/8$. We divided the experimental values into the theoretical values and in this way obtained an average multiplying factor which was then used to place the experimental values on a common basis.

Since the different contributions of O and Zn can be calculated for any particular Miller index l, the results for S_1^0 are listed in the order $l=0, 1, 2 \cdots$ in Table II. This table shows the average deviations and the comparison with theoretical values based upon a spherical electron distribution (Pauling-Sherman), and upon a distribution distorted by valence electrons (James and Johnson).

Computed intensities of the lines are affected, of course, also by the choice of the parameter, u. Assuming atom factors calculated from a spherical charge distribution, values of S_1^2 have been calculated as a function of the parameter between the limits $0.36 < u < 0.39$. The changes in intensity, for a range of ± 0.005 in the parameter, are not greater than the average deviations in the observed intensities, and no uniform improvement of the results is obtained by introducing a parameter deviating markedly from 0.375.* In comparing the experimental values with the ones calculated from a spherical charge distribution and with the results of the calculations for an asymmetrical distribution of electrons, one sees that the experimental results are in better agreement with the distorted charge distribution. This becomes still more evident from Fig. 2 which shows the experimental x-ray values as compared with the theoretical calculations. In comparing these results we see that while the spherical distribution gives one curve only for $l=3$, and $l=5$, and for $l=2$ and $l=6$, the distribution of the valence electrons produces a splitting of these curves. Still more striking is the displacement of $l=3$ and of $l=2$ with respect to $l=0$.

TABLE III. *Comparison of experimental electron diffraction values of S_{1e} with values obtained from x-ray data*
$$S_{1e}=Z_{\mathrm{Zn}}-F_{\mathrm{Zn}}+(Z_{\mathrm{O}}-F_{\mathrm{O}})e^{2\pi i u l}$$
$$Z_{\mathrm{Zn}}=30,\ Z_{\mathrm{O}}=8,\ u=3/8.$$

hkl	$Z_{\mathrm{Zn}}-F_{\mathrm{Zn}}$	$Z_{\mathrm{O}}-F_{\mathrm{O}}$	S_{1e} CALCULATED FROM X-RAY DATA	S_{1e} EXPT. VALUES
100	3.2	2.35	5.5	3.8
110	8.	4.15	12.2	9.4
200	11	4.65	15.6	12.1
120	14.9	5.6	20.5	18.9
300	16.5	5.95	22.4	21.4
220	19.1	6.25	25.35	18
101	6.9	2.8	5.3	3.4
201	13.7	4.8	10.85	8
211	16.3	5.65	12.9	10.6
002	5.7	2.6	6.3	4.7
102	7.7	3.65	8.5	8.4
112	14.7	4.75	15.4	11.1
202	13.9	5.1	14.7	13.1
212	16.4	5.8	17.4	16.7
302	17.7	6.1	18.8	18.4
103	11.5	4.5	15	14.7
203	16.4	5.5	20.6	16
213	17.9	6.0	22.7	19.1
004	12.3	4.85	7.5	12.8
104	15.1	5.3	9.8	12.8
114	16.1	5.75	10.4	12.9
204	15.6	5.9	9.7	14
214	18.7	6.2	12.5	13.3
105	17.8	5.85	22.3	22.4
205	19.1	6.2	23.8	22.7
006	18.1	6.15	19.1	18
106	20	6.2	20.9	19.4

Two distributions of the valence electrons have been considered, in which either two or three of the valence electrons were placed in a prolate ellipsoid along the c axis and the remaining two or one were distributed at random. The general character of the observed intensities is represented better by the curves obtained from the model assuming two valence electrons (particularly at large values of $\sin\theta/\lambda$). While the

---

* As seen from Table I of Johnson's paper, this issue, the main difference between the valence electron model, accounting for our results, and the spherical distribution is in the slope of the curve for $l=0$, which is independent of the parameter μ.

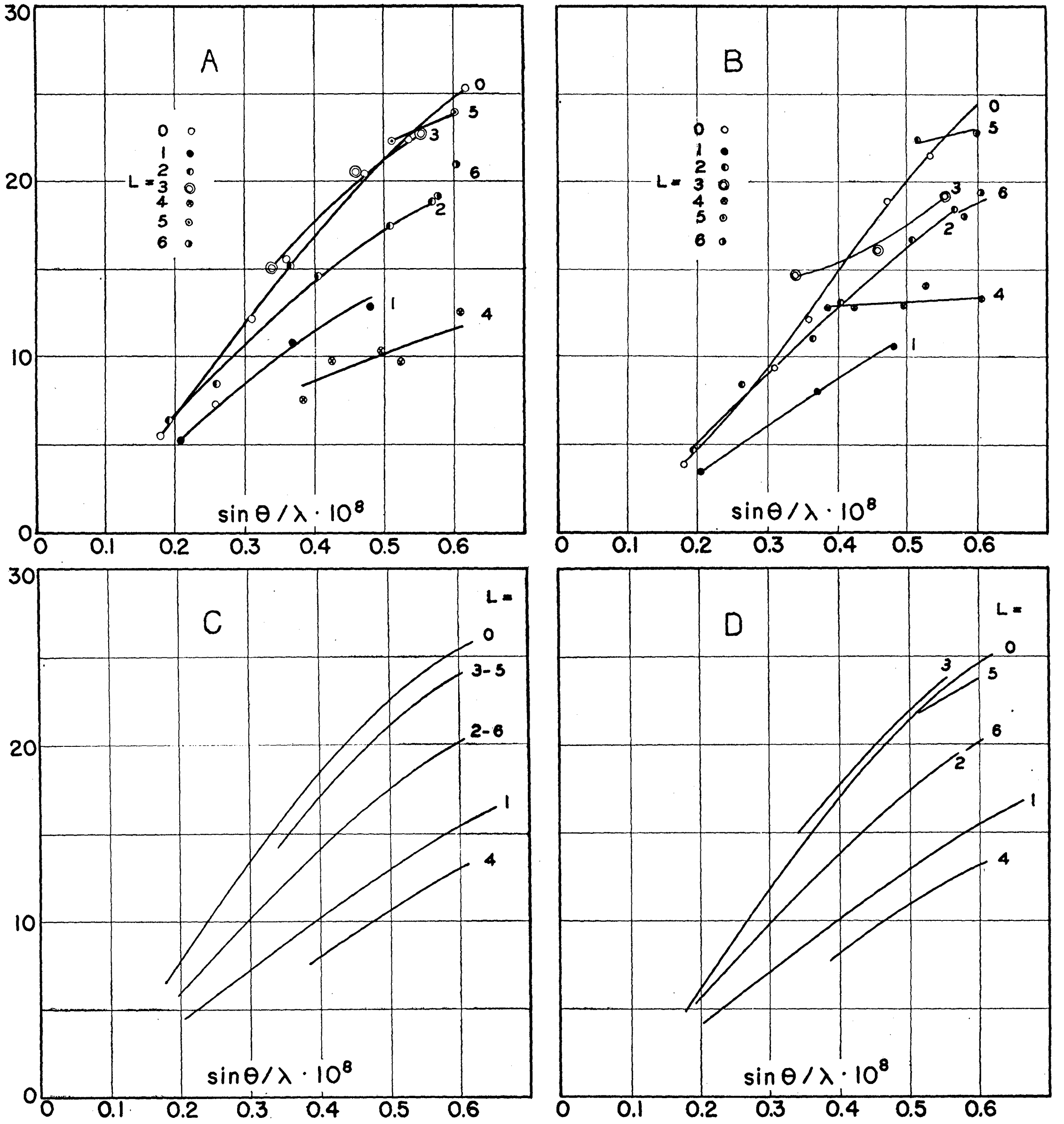

FIG. 3. Electron diffraction structure factor S_{le}' for the zinc oxide molecule. A. Derived from experimental x-ray data; B. Determined experimentally by electron diffraction; C. Theoretical curves calculated from spherically symmetric electron distribution (Pauling-Sherman); D. Theoretical curves calculated from an ellipsoidal distribution of 2 of the valence electrons (James and Johnson).

assumed deviations from spherical distribution reproduce the experimental curves, in the main, there are still some anomalies, particularly in the intensities of the lines corresponding to $l=5$ and $l=4$. The line belonging to $l=4$ should be much lower in respect to $l=1$ than is actually observed. We will discuss this point in greater detail in connection with the electron diffraction curves.

(b) Comparison of x-ray and electron diffraction scattering curves: derived electron *F* factors

The quantitative evaluation of the x-ray intensities reveals anomalies which can be explained in the main by the assumption of a quasi molecular binding in the crystal, but the differences are so small that one would hesitate to postulate, on this basis alone, the existence of a distortion due to bonding.

The electron diffraction pattern, however, shows a behavior which cannot be reproduced to any extent by the assumption of a spherical electron distribution. It is then the combination of x-ray and electron diffraction investigations which makes it possible to recognize small changes in electron distribution. They appear as anomalies in the intensities of the electron diffraction pattern and can be diagnosed by investigating the corresponding x-ray pattern.

The electron diffraction structure factor for the ZnO molecule, S_{1e}, is given by

$$S_{1e}=(Z_{\mathrm{Zn}}-F_{\mathrm{Zn}})+(Z_{\mathrm{O}}-F_{\mathrm{O}})e^{2\pi iul}.$$

In order to make a detailed comparison of the x-ray results with those obtained from electron diffraction, we have solved the corresponding equation for x-rays:

$$S_1=F_{\mathrm{Zn}}+F_{\mathrm{O}}e^{2\pi iul}$$

for values of F_{Zn}, using the theoretical spherical distribution values of the atom factor for O and the experimental x-ray values of S_1.[15] To these values we add the atom factor defect due to the use of Cu $K\alpha$ radiation, to obtain an experimental value of the atom factor for Zn in the ZnO lattice. Using these atom factors for Zn we constructed the electron diffraction factor S_{1e} as defined above.[16]

The results of these calculations are shown in the Table III, together with the experimental electron values, which have been normalized in the same manner as the x-ray values. The Figs. (3A and 3B) show the electron diffraction factor S_{1e} as obtained from x-ray data and the experimental electron diffraction results.

A comparison of Fig. 3A with Fig. 3B shows that it is possible to reproduce the main features of the electron diffraction pattern from x-ray data.[17] In both cases the curves for $l=2$, 3, 5, cross the curve for $l=0$, and $l=2$ and $l=6$ lie on separate curves.

7. Discussion

The satisfactory agreement between the scattering curves obtained directly from electron diffraction and those derived from experimental x-ray atom curves, shows that the explanation of the anomalous intensities as produced by scattering from an asymmetric charge distribution is essentially correct. At the outset it is surprising that the x-ray intensities estimated by visual inspection, or from a microphotometer trace, seem to be normal, whereas the electron diffraction intensities are, even visually, entirely different from what the structure factor would lead us to expect. In the light of our results the cause of this apparent discrepancy becomes clear. It is evident that even monotonous x-ray S curves can produce a crossing over in the corresponding electron diffraction curves. Such an effect is produced if the valence electrons are distributed in an ellipsoidal fashion as in the model calculated by James and Johnson.

Figures 3C and 3D show the theoretical electron scattering curves as obtained from the assumption of a symmetrical charge distribution and from a model assuming an asymmetric distribution as discussed before. The principal characteristics of the experimental results are reproduced only in the curves obtained from the asymmetric charge distribution.

In comparing the experimental values as derived from x-ray scattering with the theoretical curves, one finds that the experimental value for $l=5$ lies closer to $l=0$ than $l=2$, and $l=3$ lies somewhat lower than the theoretical curve. This shift of the experimental curve is, however, in agreement with the experimental electron diffraction curves of Fig. 3B. That the curve for $l=3$ does not intersect the curve for $l=0$ as found experimentally is due to the model chosen in the theory. The charge distribution ρ is a function of Z only.† While the distortion of the valence electron distribution gives an adequate

---

[15] This procedure is justified by the fact that the O has a much smaller effect than the Zn. If one calculates the atom factor of O from the experimentally observed scattering power, using James' and Johnson's calculations for Zn, one obtains unreasonable results. This is due to the fact that such an interpretation puts all experimental errors into O.

[16] This procedure is strictly correct only if the electron cloud is spherically symmetric. Any asymmetry will introduce a small phase factor in the electron diffraction calculation. Trial calculations, using a graphical method have shown, however, that the error made in this simplification is less than the experimental error.

[17] The similar procedure: calculating theoretical x-ray atom factor from the electron diffraction data is subject to much greater error. See reference 18.

† See Section II, Part 3 of Johnson's paper, this issue.

explanation for the main trend of the picture, there are still some anomalies which remain unexplained. Such anomalies occur mostly at large values of $\sin\theta/\lambda$. The electron diffraction curve for $l=3$ lies much higher as compared with $l=1$ than does the one from x-ray results. The two points for $l=6$ do not permit an accurate determination of the curve on account of the very weak[18] intensity of the reflections for $l=6$, but they are high in respect to $l=2$ whereas the corresponding electron diffraction values are low.

To understand these remaining discrepancies between theory and experiment a more detailed discussion is necessary. The ellipsoidal distribution of the valence electrons determines the slope for the different curves and thus produces the crossing over of the S curves for different values of l, in agreement with the experimental results. If, however, we consider the position of separate points along one of the curves, then we frequently find that the position of the x-ray and electron diffraction points are displaced in opposite direction with respect to the average curve itself. For a certain plane (hkl) we find that an x-ray point with high intensity, with respect to the average curve, corresponds to an electron point with low intensity. Such points are all those belonging to $l=4$ (x-ray 004 low, 104 high, 204 low, 214 high; electron 004 high, 104 low, 204 high, 214 low). Other such points are 203, 102.

Since the intensities in electron diffraction depend on $(Z-F)^2$, and the x-ray intensities on F^2, we see that any effect which influences these intensities in the same direction will produce errors of opposite sign in the F values deduced from them. Any effect such as preferred orientation, preferred crystal growth, impurities, temperature disturbance, or a state of order-disorder in the crystal, which changes the structure factor, could produce such a result. We conclude that the residual differences between the F values deduced from the charge distributions and those deduced from intensity measurements are not due principally to imperfections in the assumed charge distribution, but to some factor affecting x-ray and electron intensities in the same direction.

As already mentioned,[1] impurities and preferred orientation are not responsible for any of the observed anomalies. The effect of crystal form due to the methods of preparation was considered. We have investigated powder obtained from single ZnO crystals by crushing, but did not find any deviation from the patterns obtained from ZnO powder made by other methods. The effect of anisotropic heat motion cannot be completely excluded before x-ray measurements have been made. Preliminary electron diffraction experiments[13] at liquid-air temperature, room temperature and above 350°C show, however, that the same intensity anomaly exists at all temperatures without any appreciable change, indicating that the temperature correction cannot be the main reason for the remaining discrepancies.

Although zinc oxide is an insulator at ordinary temperatures, it becomes electrically conducting at elevated temperatures. This conductivity is of the electronic type, indicating a tendency to a state of disorder in the crystal. Such a disorder would influence x-ray and electron patterns in the same way and in the calculation of F would therefore produce an apparent inversion of the different points in respect to the main curve as we have observed.[19] Intensity anomalies found in silver iodide, which has a structure similar to zinc oxide, (Wurtzite) have been explained primarily on the basis of order-disorder.[20] In some of the x-ray investigations in alloys it is not quite clear how far order-disorder or the possible effect of a distortion of the electron cloud will determine the intensities.

It would seem that the combination of x-ray and electron diffraction investigations points the way to the possibility of determining the cause of observed intensity anomalies. Anomalies due

---

[18] The determination of the weak intensities is, however, less uncertain in the x-ray pattern than in the electron diffraction pattern as can be seen by an examination of the electron diffraction microphotometer trace. (Fig. 1). The diffraction peaks in this case are much broader, ovelap to a greater extent, and are superimposed upon a rather steep background. The construction of this background is somewhat arbitrary.

[19] Depending upon the type of order-disorder, it is also possible, as has been pointed out recently by L. H. Germer and F. E. Haworth, Phys. Rev. **56**, 212 (1939), ordering effects appear in the electron diffraction, but not in the x-ray pattern due to the different size of the domain investigated. This, however, does not apply in the case of vagabond ions as assumed here.

[20] L. Helmholtz, J. Chem. Phys. **3**, 740 (1935).

to structural properties would influence x-ray and electron diffraction in the same way, and therefore, produce in the F curve an apparent inverted behavior. The anomalies due to an intrinsic change in the electron cloud of the atom due to bonding, or anisotropic lattice distortions, since they affect primarily the F factor, would not cause difficulty in reproducing electron diffraction curves from x-ray experiments.

To investigate the remaining discrepancies from this point of view we have started experiments at different temperatures, using ionization methods to refine the technique of intensity measurements.

The present experiments alone do not allow a a definite decision as to order-disorder in the zinc oxide crystal. It is possible, however, to derive the type of binding from the F factor curves for electron diffraction and x-rays combined and to separate the effects of electron cloud distortion from those of structural factors which change both electron diffraction and x-ray intensities in the same direction.

We wish to thank Professors James and Yearian, and Dr. Johnson for many interesting discussions; we wish also to thank Dr. R. K. Waring of the New Jersey Zinc Company for the gift of the spectroscopically pure zinc from which the zinc oxide has been prepared.

APRIL 1, 1940 PHYSICAL REVIEW VOLUME 57

The Effect of Valence Electrons and Electron Cloud Distortion upon Intensities in Electron and X-Ray Scattering*

(Applied to Zinc Oxide)

VIVIAN A. JOHNSON
Purdue University, Lafayette, Indiana

(Received December 28, 1939)

An extensive investigation of electron scattering by zinc oxide has been carried out by Lark-Horovitz and Yearian. The intensity distribution, determined by photographic methods, showed marked anomalies with respect to the intensity distribution of the corresponding x-ray pattern. The visually estimated x-ray intensities seem to be in general agreement with values calculated from approximate Fermi or Pauling-Sherman wave functions, and the marked anomalies appear only in the electron diffraction pattern. The observed intensities have been formally accounted for by assuming a polarization of the M shell of the zinc atom. This hypothesis has been tested by calculating the charge distribution of the M shell in zinc under the effect of the electrostatic fields arising from a partly ionic character of the lattice and its deviation from perfect tetrahedral symmetry. The calculated distortion is too small by a factor of $1/60$ to account alone for the observed anomalies. Then the effect due to the valence electrons is considered. A rough agreement with experimental values is obtained with a model in which two valence electrons of each zinc-oxygen pair of nearest neighbors are assumed to be placed in a uniform linear distribution between these neighboring nuclei and the other two in a uniform distribution through the crystal. A more refined model, in which two valence electrons of each zinc-oxygen pair of nearest neighbors are assumed to be distributed over the surface of an ellipsoid with major axis axis along the c axis of the crystal, accounts for the principal anomalies in the electron diffraction intensities, and at the same time gives results which are in agreement with measured x-ray intensities. The importance of the method used as a tool for determining the type of binding in a crystal is discussed.

INTRODUCTION

A LARGE number of electron diffraction patterns of zinc oxide have been obtained by Lark-Horovitz and Yearian.[1, 2] The intensity distribution was determined by the photographic method and was found to show marked anomalies with respect to the corresponding x-ray pattern. The scattering of x-rays is not influenced by the nucleus of the scattering atom, but electron diffraction is affected by both the nucleus and the electronic cloud. Therefore it should be possible to use electron diffraction to locate the positions of nucleus and electrons in a crystal lattice. It was for this reason that Yearian and

---

* The investigation reported here is based in part upon a doctoral thesis submitted to the Faculty of Purdue University.

[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] H. J. Yearian, Phys. Rev. **48**, 631 (1935).