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X-Ray Dispersion and Atomic Electron Cloud Distortion in Zinc Crystals

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Monochromatic x-rays of wave-lengths 1.54A (Cu $K\alpha$) and 1.433A (Zn $K\alpha$) were diffusely scattered at angles ϕ varying from 24° to 120° from single crystals of zinc ($\lambda_K=1.28$A) whose orientation angles ψ were 0° and 90°. The intensity of the diffusely scattered rays was found to vary with $(\sin \frac{1}{2}\phi)/\lambda$ according to Jauncey's theoretical formula for the region of wave-lengths close to the K critical absorption wave-length of the scattering crystal. In the case of the scattering of Cu $K\alpha$ rays the decrement Δf in the atomic structure factor was 2.5 as compared with Hönl's value of 2.3. For the less intense Zn $K\alpha$ rays Δf was 3.65 as compared with Hönl's value of 2.8. The difference in the latter case is probably due to experimental error. More interesting was the "dip" or "valley" found in the diffuse scattering $S(\psi=0°)$ values in the region of $(\sin \frac{1}{2}\phi)/\lambda=0.3\text{A}^{-1}$. After considering various possible causes for this dip, it was finally decided that the cause of the dip is a corresponding dip in the atomic structure factor $f(\psi=0°)$ values in this region. The maximum difference, $f(\psi=90°)-f(\psi=0°)$ is about 6 electrons. This is greater than the previous value of 2.4 electrons and indicates a larger and deeper distortion of the electron cloud of a zinc atom in the crystal than had previously been imagined.

I. Introduction

Jauncey[1] has recently extended the theory of diffuse scattering of x-rays by crystals to the case where the wave-length of the primary rays is longer than the K-critical absorption wave-length of the crystal. The extended theory shows that in the formula for S the change in the incoherent portion is negligible and that the atomic structure factor f in the coherent portion is replaced by $f-\Delta f$ where Δf is the decrement in f due to anomalous dispersion. Hence the theoretical value for S in the region of a K-absorption edge is

$$S=(f-\Delta f)^2(1-e^{-2M})/Z+[1-(1/Z)\Sigma E_r{}^2]/R, \quad (1)$$

where $R=(1+h \text{ vers } \phi/mc)^3$. For a hexagonal crystal like zinc, Zener[2] has shown that

$$M=(a\cos^2\psi+b\sin^2\psi)\cdot(\sin\tfrac{1}{2}\phi)^2/\lambda^2, \quad (2)$$

where ψ is the orientation angle.[3] For zinc[4] at room temperature, $a=2.34\text{A}^2$ and $b=0.68\text{A}^2$.

The original purpose of this investigation was to study the effect of anomalous dispersion on the diffuse scattering of x-rays and to measure the decrement Δf in the atomic structure factor, since Δf values had not been previously determined directly by diffuse scattering methods. Heretofore all experiments on the diffuse scattering of x-rays from zinc crystals had been done with general radiation of an average wave-length of about 0.44A which is much shorter than 1.28A, the K-critical absorption wave-length of zinc. In this investigation, monochromatic radiation of wave-length longer than that of 1.28A was used.

The use of general radiation has the advantage of high primary intensity, which is important because of the very low magnitude of the diffuse scattering coefficient. However, this method has the disadvantage of extreme analytical difficulty in calculating atomic structure values, involving the arithmetical solution of an integral equation.[4, 5] Furthermore there is always the possibility that fine structure effects will be so smeared out because of the range of wave-lengths used as to be indiscernible. Finally it is experimentally very difficult to make diffuse scattering measurements at small scattering angles, so that in order to study the interesting region of small values of $(\sin \frac{1}{2}\phi)/\lambda$ it is expedient to use comparatively soft x-rays, such as Cu $K\alpha$ ($\lambda=1.54$A) or Zn $K\alpha$ ($\lambda=1.433$A) radiation.

As the experiment proceeded it became evident that the distortion of the electron cloud in the

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[1] G. E. M. Jauncey, paper to be published.

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

[3] In diffuse scattering experiments the orientation angle ψ is the angle that the line bisecting the angle between the forward direction of the scattered rays and the backward direction of the primary rays makes with the c axis of the crystal.

[4] W. A. Bruce, Phys. Rev. **53**, 802 (1938).

[5] G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **51**, 1068 (1937).

zinc atom was more important than had at first been realized[4, 5] and so this research became as much an investigation of the electron cloud distortion as of the anomalous dispersion effects on the long wave-length side of the K-absorption edge of zinc.

II. Apparatus

Since the coefficient of diffuse scattering is so exceedingly small it is necessary to have both a very intense incident beam of x-rays, and a sensitive method of measuring very weak ionization currents produced by the diffuse scattering. An all-metal continuous-pumping x-ray tube was the source of x-radiation. This tube followed in construction a design by Wollan[6] and was water-cooled in order to withstand the heating produced by large electron current-densities at voltages of the order of 25 kilovolts. The vacuum system for the x-ray tube was a two-stage oil-diffusion pump backed by a Cenco Hyvac mechanical pump. This diffusion pump, designed by Professor A. L. Hughes who combined the two-stage arrangement of Henderson[7] with Hickman's[8] refluxing device, performed excellently under adverse conditions. When a dry-ice trap was used pressures of the order of 10^{-6} mm of mercury were readily maintained.

Power to operate the tube was furnished by a conventional 60-cycle transformer-Kenetron high voltage full wave rectifier capable of producing continuously 100 milliamperes at 50 kilovolts. Targets used were of copper and zinc, the latter consisting of a zinc button fused to a copper backing.

Initially a rocksalt crystal was used as monochromatizer but this was soon abandoned in favor of a cleaved zinc crystal for two reasons. First, the deliquescent property of rocksalt caused it to be attacked by moisture in the air to such an extent that the reflected x-ray line became a jumble of lines after two or three weeks. Second, and more important, the absorption coefficients of zinc for Cu $K\alpha$ ($\lambda=1.54$A) rays and for the rays of half wave-length ($\lambda=0.77$A) are 58.6 and 64, respectively, because the two wave-lengths are on opposite sides of the K-absorption edge for zinc ($\lambda=1.28$A). But with rocksalt the absorption coefficient for the Cu $K\alpha$ is roughly eight times that for the half wave-length. This means that the relative intensity of the half wave-length present in the reflected beam should be much less when zinc instead of rocksalt is the reflector. The importance of this effect will be shown later. With proper adjustment of the Seeman wedge, the $K\alpha$ and $K\beta$ lines could be seen easily on a fluorescent screen.

Measurement of the intensities of the primary and scattered x-ray beams was accomplished by means of a Cambridge type Compton electrometer in conjunction with a brass ionization chamber of 5 cm inside diameter and 8 cm length, filled with argon at atmospheric pressure. Although methyl bromide has a slightly greater absorption coefficient for the wave-lengths used, this advantage is not enough to compensate for its extremely corrosive properties. The chamber window was rectangular in shape, 2.12 cm by 0.52 cm, covered with Cellophane of thickness 2.78×10^{-3} g/cm^2, and was 11.5 cm from the spectrometer axis. This chamber is considerably smaller than those used recently in diffuse scattering work and although the background is still larger relative to the intensity of diffuse scattering than is desirable, it is an improvement in that respect over former apparatus.

Whenever the interior of the x-ray tube had been exposed to air, a process of "aging" the tube under increasingly high voltages was necessary for a period depending upon the length of time the tube had been exposed. During this process, a burst of gas occasionally caused a spark discharge within the tube and the resulting radio-frequency pulse picked up by the electrometer and ionization chamber circuit was strong enough to destroy the conducting film on the electrometer suspension. To avoid this minor catastrophe, the electrometer and its associated batteries were entirely isolated electrically by grounded metal shielding outside the electrometer casing, except for a slit through which light was focused on the electrometer mirror.

The electrometer was normally operated at a sensitivity of about 5000 mm per volt, which is a comparatively low voltage sensitivity, but, as

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[6] E. O. Wollan, Rev. Sci. Inst. **9**, 3 (1938).

[7] J. E. Henderson, Rev. Sci. Inst. **6**, 66 (1935).

[8] K. C. D. Hickman, J. Frank. Inst. **221**, 215 and 383 (1936).

noted by Neher,[9] the current sensitivity is a maximum in this region. Since the primary intensity was of the order of 10^5 times the scattered intensity, it was necessary to use a shutter which would allow the primary beam to enter the ionization chamber for one-sixtieth of a second (one period of 60-cycle a.c.)

Some measurements were made using an evacuated crystal-holder with the aim of eliminating scattering from the air, but this was found to be not sufficiently important to justify the added complication.

Single crystals of zinc used in this experiment were prepared as described by Jauncey and Bruce[10] with the difference that the crystals were etched electrolytically following the method of Vernon and Stroud.[11]

III. Experimental Method

The experimental value of the diffuse scattering as given by Jauncey and Bruce[12] is

$$S=\frac{4R^2Wm^2c^4}{ANZe^4(1+\cos^2\chi\cos^2\phi)}\times\frac{D(\phi,\theta)}{D_0u(\phi,\theta)}\times\frac{\mu_1}{\rho},\quad(3)$$

where $D(\phi, \theta)$ is the ionization current caused by the diffusely scattered rays when the ionization chamber is set at a scattering angle ϕ and the crystal face makes an angle θ with the incident rays, and where D_0 is the ionization current caused by the primary beam. It will be noted that the factor $(1+\cos^2\phi)$ as given by Jauncey and Bruce is replaced by $(1+\cos^2\chi\cos^2\phi)$. This change takes account of the polarization of the $K\alpha$ radiation reflected at a grazing angle $\chi/2$ from the monochromatizer. The remaining symbols in (1) are defined by Jauncey and Bruce.[12]

Because the output of characteristic x-radiation increases rapidly as the potential applied to the tube is raised above the excitation potential (8970 volts for Cu $K\alpha$ and 9750 volts for Zn $K\alpha$ rays), high primary intensity may be obtained by operating the tube at a relatively high voltage. However, the monochromatizer will reflect not only the $K\alpha$ radiation but also any submultiple of the $K\alpha$ wave-length. To excite wave-lengths of one-half the Cu $K\alpha$ and Zn $K\alpha$ wave-lengths in the general radiation requires peak potentials of 16,050 and 17,250 volts, respectively. Since in some cases a peak potential of 20,000 volts was used it was necessary to correct for the fluorescence radiation from the zinc crystal (critical K absorption wave-length = 1.28A).

Now the ionization current measured when x-rays are falling on the crystal of zinc is the sum of (1) background currents due to cosmic rays, alpha-particles, insulation leaks, and scattering from the air; (2) diffuse scattering of the half wave-length rays reflected from the monochromatizer; (3) fluorescent radiation from the zinc crystal excited by the half wave-length rays; and (4) diffuse scattering of the $K\alpha$ radiation. On account of the high fluorescence yield[13] it is very important to make the proper correction for the effects due to the half wave-length radiation. To illustrate, with a primary beam containing roughly one percent of half wave-length radiation, the fluorescent intensity was equal to that of the diffusely scattered $K\alpha$ radiation. To get the true $D(\phi, \theta)$, measurements were made as follows. Let B_1 be the background current for a given ϕ and θ, and let D' be the current due to the scattering of half wave-length rays and to the fluorescent radiation excited by it. Then the total current in the ionization chamber is

$$D_1=D(\phi,\theta)+D'+B_1.\quad(4)$$

Now insert a thickness t of aluminum into the primary beam and let the absorption coefficients of the $K\alpha$ rays and half wave-length rays in aluminum be μ_1 and μ_2, respectively. The ioniza-

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[9] John Strong, *Procedures in Experimental Physics* (Prentice-Hall, New York, 1938), Chapter VI (H. V. Neher).

[10] G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **51**, 1062 (1937).

[11] W. H. J. Vernon and E. G. Stroud, Nature **142**, 477 (1938).

[12] G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **50**, 413 (1936).

[13] Compton and Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, 1935), pp. 477–492. The intensity of the fluorescent scattering is inversely proportional to the sum of the linear absorption coefficients for the fluorescent and exciting radiations, and directly proportional to the fluorescence yield. Since for the case at hand the linear absorption coefficients of zinc for $\lambda = 0.77$A and for its own K radiation are relatively small, and since the fluorescence yield is about 0.5 we should expect a comparatively large amount of fluorescence radiation.

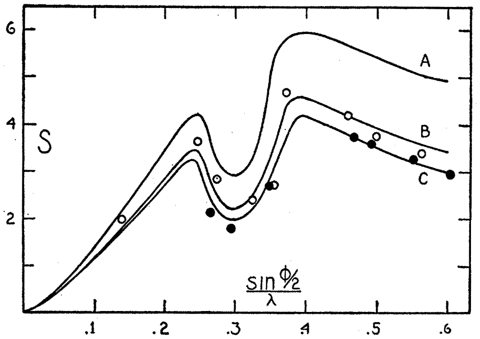

FIG. 1. S values for zinc, $\psi=0°$. Clear circles, Cu $K\alpha$ rays; black circles, Zn $K\alpha$ rays.

tion current is then[14]

$$D_2=\exp\left[-\mu_1 t\right]D(\phi,\,\theta)+\exp\left[-\mu_2 t\right]D'+B_2, \quad (5)$$

where B_2 is the background when the aluminum is inserted. Eliminating D' from (4) and (5), we obtain

$$D(\phi,\,\theta)=\{D_1-(D_2-B_2)\exp\left[\mu_2 t\right]-B_1\}/\{1-\exp\left[(\mu_2-\mu_1)t\right]\}. \quad (6)$$

The background currents B_1 and B_2 are measured by turning the crystal so that its face cannot be "seen" by the ionization chamber window. For the primary intensity D_0 we get similarly

$$D_0=\{I_1-(I_2-B)\exp\left[\mu_2 t\right]-B\}/\{1-\exp\left[(\mu_2-\mu_1)t\right]\}, \quad (7)$$

where I_1 and I_2 are the primary beam currents measured respectively without and with aluminum and B is the background.

This method was used for part of the Cu $K\alpha$ data, with the tube operated at 20 kilovolts peak and 50 ma. But with a zinc target it was not possible to use so much power because the zinc melted at the focal spot. Therefore all the Zn $K\alpha$ data (and part of the Cu $K\alpha$ data) were taken with the peak voltage ≤ 15 kilovolts, thus avoiding the necessity for correcting for the effect of the half wave-length radiation. As a matter of experience it was found to be more satisfactory to use the lower voltage than to correct for the fluorescence radiation, even though the primary beam was on this account decreased to about $\frac{1}{5}$ of that attained with the higher voltage. The reduced intensity and consequent increased length of time necessary for obtaining a single reading with the same probable error as with the higher intensity is compensated for by the fact that just two types of readings are necessary, whereas the correction method requires four. Furthermore, the correction for fluorescence introduces an additional possibility of systematic experimental error.

IV. EXPERIMENTAL RESULTS

The experimental S values as calculated by (3) are shown in Figs. 1 and 2, in which the white circles represent measurements made with Cu $K\alpha$ ($\lambda=1.54$A) rays and the black circles represent measurements made with Zn $K\alpha$ ($\lambda=1.434$A) rays. Fig. 1 is for zinc crystals with orientation angle $\psi=0°$, and Fig. 2 is for zinc crystals with $\psi=90$.

The writer wishes to point out that the "dip" or "valley" in the S curves jor $\psi=0°$ *in the region* $(\sin\frac{1}{2}\phi)/\lambda=0.3\text{A}^{-1}$ *has not previously been found.*

V. EFFECT OF ANOMALOUS DISPERSION

The curves A, B, and C of Fig. 1 except in the region $0.25\text{A}^{-1}<(\sin\frac{1}{2}\phi)/\lambda<0.4\text{A}^{-1}$ were calculated from (1) on the basis of Bruce's[4] $f(\psi=0°)$ values with $\Delta f=0$, 2.5, and 3.3, respectively. The curves D, E, and F of Fig. 2 were calculated on the basis of Bruce's $f(\psi=90°)$ values over the whole region with $\Delta f=0$, 2.5, and 4.0. It will be seen that the experimental points fall reasonably well on the theoretical curves. The value 2.5 of Δf for Cu $K\alpha$ on zinc ($\lambda/\lambda_K=1.2$) is particularly gratifying in that it is reasonably close to Hönl's value[14] of 2.3. The average 3.65 of the two values 3.3 and 4.0 for Zn $K\alpha$ on zinc ($\lambda/\lambda_K=1.1$) is greater than Hönl's value of 2.8. The Zn $K\alpha$ rays

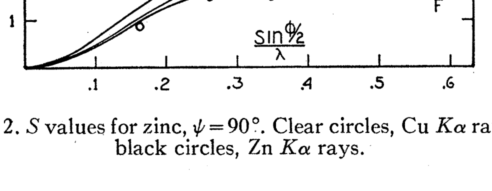

FIG. 2. S values for zinc, $\psi=90°$. Clear circles, Cu $K\alpha$ rays; black circles, Zn $K\alpha$ rays.

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[14] H. Hönl, Ann. d. Physik **18**, 625 (1933). See also W. A. Bruce, reference 4.

were much less intense than the Cu $K\alpha$ rays and the values 3.65 and 2.8 probably do not differ by more than the experimental error.

A collection of values for Δf obtained by different investigators is shown in Fig. 3. This diagram is taken from papers by Allison and Jesse[15, 16] with the points obtained by the writer added. It is seen that the experimental values form a kind of cloud about Hönl's theoretical curve. Perhaps the best that can be said in this connection is that the Δf values obtained by diffuse scattering like the values obtained by other methods show the necessity of taking account of anomalous dispersion in the region of λ/λ_K near unity.

The importance of taking account of Δf in diffuse scattering is shown by the curves A and D in Figs. 1 and 2, which were calculated on the basis of no dispersion ($\Delta f=0$). The departure of the experimental points from these curves is beyond doubt and the writer believes that the experimental evidence supports Jauncey's theoretical equation (1).

VI. Attempts at Explanation of Dip in the $S(\psi=0°)$ Curve

(a) Experimental error

At the close of Section IV the reader's attention was drawn to the existence of a "dip" in the experimental S ($\psi=0°$) curves. When Bruce's f values are used in (1) no such dip appears. At first it was thought that the low S values in the region of $(\sin\frac{1}{2}\phi)/\lambda=0.3\text{A}^{-1}$ might be due to experimental error and these S values have consequently been determined again and again with various crystals but they always exhibit the same behavior as shown in Fig. 1. The reality of the existence of the dip being established, the question arises as to its explanation.

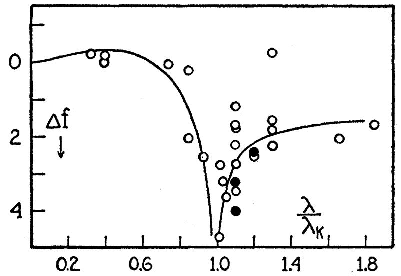

Fig. 3. Values of Δf. Clear circles, results from previous reflection measurements; black circles, results from diffuse scattering measurements; curve, Hönl's theory.

The theory of diffuse scattering is well established only in those regions where the angle of scattering is not too close to the direction in which a Laue spot occurs. Therefore in making determinations of S values it is necessary to be far enough from the position of a Bragg reflection so that the readings are independent of θ when they are divided by

$$u(\phi,\theta)=\frac{2\sin(\phi-\theta)}{\sin(\phi-\theta)+\sin\theta},\tag{8}$$

where ϕ is the angle of scattering and θ is glancing angle of the x-rays on the surface of the crystal. Because of the width of the ionization chamber window and of the defining slits for the primary beam, it is a matter of experience that the scattering angle should differ from twice the Bragg angle for reflection by approximately four degrees or more. All observations made fulfilled this condition.

(b) Laval's discontinuities

In 1937 Laval[17] reported discontinuities in the diffuse scattering of Cu $K\alpha$ rays from powdered crystals in the region between a scattering angle of zero and a scattering angle less than twice the Bragg angle corresponding to the smallest angle of reflection. It was a disconcerting fact that one of the discontinuities found by Laval for powdered nickel occurred at $(\sin\frac{1}{2}\phi)/\lambda$ close to 0.3A^{-1}. Since, according to Laval, the $(\sin\frac{1}{2}\phi)/\lambda$ for a given discontinuity is a function of the atomic number, there should be a discontinuity for zinc in this region. However, Harvey[18] has shown that Laval's discontinuities for aluminum can all be explained on the basis of reflections of submultiples of the Cu $K\alpha$ rays from the powdered aluminum. In Table I are shown values of $\sin\frac{1}{2}\phi$ for Laval's reported discontinuities for aluminum. In the second row of the table are shown the values calculated according to Harvey's

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[15] S. K. Allison and W. P. Jesse, Phys. Rev. **49**, 483 (1936).

[16] W. P. Jesse, Phys. Rev. **52**, 443 (1937).

[17] J. Laval, Comptes rendus **201**, 889 (1935).

[18] G. G. Harvey, Phys. Rev. **55**, 1147 (1939).

suggestion. In the third row are shown the respective reflections[19] of submultiples of the Cu $K\alpha$ wave-length. Thus (111)/3 means the (111) reflection of the wave-length (1.54/3)A from powdered aluminum. The figures in the second row of this table agree so well with those given by Laval (first row) that the writer feels with Harvey that the discontinuities claimed by Laval do not exist for pure Cu $K\alpha$ rays. Hence the writer has been forced to discard any explanation of the dip on the basis of Laval's discontinuities.

(c) Error in fluorescence correction

Since the unexpectedly low values of S occurred at approximately the value of ϕ for which a third-order Bragg reflection for the half-wave-length would occur, it was thought possible that there might be an error in the correction for the half-wave-length radiation present in the primary beam. For, if the correction factor for the half-wave-length radiation were too large, then a Bragg reflection of this radiation would result in a low S value because of over-correction. To remove this possibility the potential across the x-ray tube was reduced below the excitation potential for the half-wave-length. However, even with the lower operating voltage, when no correction for the half-wave-length rays was needed, the low S values persisted. The presence of uncorrected half-wave-length rays would of course result in a high S value. Consequently this explanation had to be discarded.

(d) Variation of electrometer sensitivity

When an electrometer set on the axis of a spectrometer is used, it is always possible that there is a variation of the sensitivity of the apparatus with different angular positions of the ionization chamber. This possibility was tested by placing a radon tube on the ionization chamber and checking the sensitivity at various values of ϕ. No such variation in sensitivity was found. Furthermore the $\psi=90°$ values of Fig. 2 show no dip comparable in magnitude with that shown by the $\psi=0°$ values.

TABLE I. *Laval's discontinuities for aluminum.*

Laval ($\sin\frac{1}{2}\phi$)	0.085	0.110	0.130	0.178	0.236	0.282
Harvey ($\sin\frac{1}{2}\phi$)	0.083	0.110	0.135	0.180	0.234	0.278
Reflection	(111)/4	(111)/3	(220)/4	(220)/3	(422)/4	(331)/3

(e) Extinction

In 1922 Jauncey[20] in the first experimental investigation on diffuse scattering looked for a change in the diffuse scattering of monochromatic x-rays in a direction ϕ when the glancing angle θ of the primary rays on the crystal was passed through a Bragg reflection value θ_B with $\phi\neq 2\theta_B$. It was felt that the apparent increase of absorption of the x-rays in the crystal (which is now known as extinction) might result in a decrease of the diffuse scattering. Jauncey was unable to find any such effect.

However, if such an effect exists, the low S values could be explained on such a basis. It was therefore thought worthwhile to test Jauncey's idea again. The Bragg angle of incidence for the (0002) reflection ($\psi=0°$) of Cu $K\alpha$ rays from zinc is 18° 15′. The ionization chamber was set at $\phi=60°$ and the crystal turned so that θ passed through 18° 15′. No decrease in the reading could be found for $\theta=18°\ 15'$. This same result was obtained with $\phi=100°$. It might be, however, that we were not obtaining the strongest possible reflection from the zinc crystal. In order to test this possibility the experiment of Bragg, James and Bosanquet[21] was repeated using the reflection rather than the transmission method. The ionization chamber was set at an angle ϕ equal to twice 18° 15′ and measurements were made with values of θ passing through 18° 15′. The results are shown in Fig. 4. The intensity of the incident beam was measured with the shutter mentioned before. The area under the curve represents what is known as the integrated intensity. This divided by the primary intensity gives $E\omega/P_0$ in the notation of Compton and Allison.[22] The ratio of the experimental to the theoretical value of

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[19] The (h, k, l) reflection from a face-centered cubic crystal like aluminum is given by

$$(\sin\tfrac{1}{2}\phi)/\lambda=(h^2+k^2+l^2)^{\frac{1}{2}}/2a,$$

where h, k, l are all even or all odd integers. For aluminum $a=4.04$A.

[20] G. E. M. Jauncey, Phys. Rev. **20**, 405 (1922). Figs. 2 and 6 should be interchanged in this reference.

[21] W. L. Bragg, R. W. James, and C. H. Bosanquet, Phil. Mag. **42**, 1 (1921).

[22] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (Van Nostrand, New York, 1935), p. 424 *et seq.*

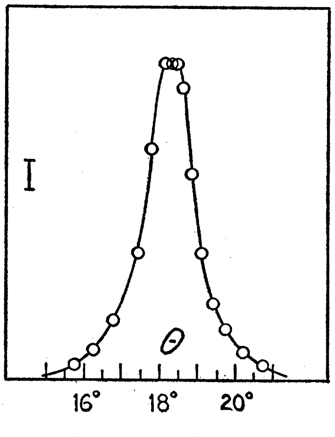

FIG. 4. Integrated intensity of (0002) reflection of Cu $K\alpha$ from a single crystal of zinc.

$E\omega/P_0$ is $\mu/(\mu+gQ)$, where μ is the absorption coefficient and gQ the extinction coefficient of the Cu $K\alpha$ rays in the zinc crystal. The ratio found was 1.59. This compares well with the value of 1.52 found by Bragg, James and Bosanquet[21] for Rh $K\alpha$ x-rays reflected in the first order from the (100) planes of rocksalt. This shows that the reflected intensity of Cu $K\alpha$ rays from the zinc crystal in this experiment was as strong as could be gotten.

The above test was necessary because of the possibility of passing unwittingly through a position for a Bragg reflection from planes other than the cleavage (0002) planes. Such a reflection would not necessarily be in the plane of scattering. To test this possibility measurements were made with the crystal face turned to different angles in its own plane; no change in the low S values was found.

VII. DISTORTION OF ELECTRON CLOUD

The writer was finally forced to the conclusion that the low $S(\psi=0°)$ values are due to low atomic structure factor values in this region of $(\sin\frac{1}{2}\phi)/\lambda$. In Fig. 1 the curves in the region $0.25\text{A}^{-1}<(\sin\frac{1}{2}\phi)/\lambda<0.4\text{A}^{-1}$ have been plotted with the use of the f values shown in Table II and also shown in Fig. 5. It is seen that the experimental points now fall reasonably well on the theoretical curves, and that therefore the explanation of the dip in the $S(\psi=0°)$ curves is a corresponding dip on the $f(\psi=0°)$ curve. This latter dip is a result of a distortion of the electron cloud of the zinc atom. The greatest difference of the $f(\psi=0°)$ and the $f(\psi=90°)$ values is from Fig. 5 about six electrons. Although the writer does not maintain that this value is exact he does believe that the maximum difference in the two f values is considerably greater than 2.4, the greatest value previously reported by workers in this laboratory.[4, 5] This large difference implies that the forces holding a zinc crystal together in its hexagonal structure affect electrons which are lower down in the atomic structure than the valence electrons.

Although in Fig. 2 the experimental value for $S(\psi=90°)$ at $(\sin\frac{1}{2}\phi)/\lambda=0.35\text{A}^{-1}$ for Zn $K\alpha$ on zinc is slightly lower than the theoretical curve, and might possibly indicate a slight dip in the $f(\psi=90°)$ curve, the writer does not believe that the present experimental evidence warrants such a dip in the $f(\psi=90°)$ curve and no such dip is shown in Fig. 5.

Further evidence of a large value of the difference between $f(\psi=0°)$ and $f(\psi=90°)$ was reported at the Thanksgiving Meeting of the Physical Society in 1937 by Wollan.[23] According to Wollan a difference of about ten electrons was found for powdered crystals of a cadmium-silver alloy, which also has a hexagonal crystal structure. At the time of the meeting such a high difference was disturbing, but the writer feels that this large difference is probably due to a similar distortion of the electron clouds of the cadmium and silver atoms making up the crystalline alloy. Similar results were obtained by Howard[24] for powdered crystals of a copper-zinc alloy, although he does not attribute the large difference in f values entirely to electron cloud asymmetry.

In previous papers describing the work on zinc crystals in this laboratory the $\psi=0°$ curves were calculated for continuous general radiation and on the assumption of f values without the dip

TABLE II. *Structure factors for zinc.* $\lambda/\lambda_K\rightarrow 0$.

$(\sin\frac{1}{2}\phi)/\lambda$	0.250	0.275	0.300	0.325	0.350	0.375	0.400
f for $\psi=0°$	20.7	16.3	14.6	14.5	16.0	18.0	17.5

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[23] E. O. Wollan, Phys. Rev. **53**, 203 (1938). This statement was made at the meeting, but is not reported in the abstract.

[24] R. A. Howard, Phys. Rev. **53**, 966 (1938). This paper also includes Wollan's f values mentioned above.

shown in Fig. 5. The effect of using the f values in Fig. 5 on the recalculated curves of the previous papers is negligible for scattering angles equal to or greater than 20°. For scattering angles less than 20° the new $f(\psi=0°)$ values do cause the theoretical $(S\rho/\mu_1)_{\text{ave}}$ curve to fall slightly below that shown, for instance, in Fig. 1 of Jauncey and McNatt's recent paper.[25] This illustrates the remark made in the introduction concerning the smearing-out of fine structure effects when general radiation is used. It is gratifying to note that the experimental point at $\phi=15°$ shown in the figure just mentioned is in somewhat better agreement with the new theoretical curve.

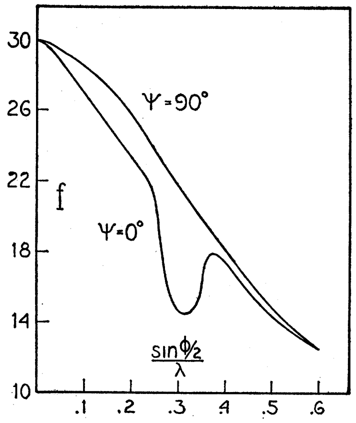

FIG. 5. Atomic structure factors for zinc $(\lambda/\lambda_K \rightarrow 0)$.

VIII. CONCLUSION

The research reported in this paper is the first to show directly the effect of the anomalous dispersion of x-rays upon diffuse scattering and to measure the decrement in the atomic structure factor by this method. Jauncey's extension of the theory of diffuse scattering to include the effects of anomalous dispersion in the region $\lambda/\lambda_K \approx 1$ (Eq. (1)) has been shown to agree with experimental results for $\lambda/\lambda_K = 1.1$ and 1.2. Finally, and most important, the results indicate a much greater distortion of the electron atmospheres of the atoms in a zinc crystal than had previously been imagined. The dip in the $S(\psi=0°)$ values and the consequent dip in the atomic structure values for $\psi=0°$ are results which former diffuse scattering experiments on zinc could not have been expected to yield because of the use of general radiation. The writer also wishes to emphasize that these new results could not possibly have been obtained by crystal reflection methods because there is no $\psi=0°$ reflection for zinc between $(\sin\frac{1}{2}\phi)/\lambda = 0.203$ and 0.406A^{-1} (0002 and 0004 reflections, respectively), which values just bridge the region of low atomic structure factors. This illustrates the advantage of the diffuse scattering method, in which all values of the scattering angle except those corresponding to Bragg reflections may be investigated.

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[25] G. E. M. Jauncey and E. M. McNatt, Phys. Rev. **55**, 498 (1939).