The Experimental Verification of the Quantum-Mechanical Dispersion Theory by Reflection and Diffuse Scattering of X-Rays from Zinc

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Hönl used his dispersion theory to develop a formula for the x-ray scattering power of an atom for wave-lengths near the absorption edge. He expressed his formula as the difference Δf between his value and f calculated by some method such as that of Hartree. In this paper it is shown that the F values obtained in the powder crystal experiments of Brindley, Wollan and Harvey, and Miller may be used to verify this formula when they are corrected by the proper temperature factor given by recent experiments in diffuse scattering. The diffuse scattering experiment also gives f values which may be used to verify the Hönl theory. It is shown that all existing data on the f values of zinc are in good agreement when they have been corrected by the Jauncey and Bruce temperature factor and the Hönl Δf. A working formula for Hönl's Δf for any element and for any wave-length is given together with a table of theoretical values of Δf for zinc. From a consideration of all experimental results for zinc a set of f values has been constructed and these are given in a table. This table shows that there is electron distortion and reasons are advanced for believing that the distortion of the electron atmosphere extends deeper into the atom than the valence electrons.

1. INTRODUCTION

THE study of the scattering of x-rays by matter has been considerably delayed by the difficulty of separating the contributing factors in the intensity measurements of the scattered x-rays. In the ideal case of the Thomson scattering from a group of free electrons, the scattered intensity at an angle ϕ with the primary beam is independent of the variable $(\sin \frac{1}{2}\phi)/\lambda$. The grouping of these same electrons into the tightly bound formation of the atom introduces a function of $(\sin \frac{1}{2}\phi)/\lambda$ by virtue of the fact that there are definite space relations among the electrons. However, the complications due to these relations are not nearly so troublesome as the difficulties caused by the natural vibrations of the electrons, for the phase angle of a scattered wave from an electron is a function of the difference between the frequency ν of the primary radiation and the natural frequency ν_e of the electron in the atom. On the classical picture, if ν is much greater than ν_e, the scattered radiation is practically in phase with the primary radiation. If ν is slightly less than ν_e, the scattered ray is approximately 180° out of phase with the primary ray. Between these limits any value of the phase angle is possible. Thus all scattering experiments which will be free from the influence of this phase change must be made with a primary radiation whose frequency is much larger than any of the natural frequencies of the electrons. Practically, this means $\nu \gg \nu_K$, where ν_K is the natural frequency of the K electrons.

Hartree[1] and other wave mechanists have calculated the scattering factor of an atom for $\nu \gg \nu_K$. They have obtained values which give better agreement with experiment than the simple classical theories. Hönl[2] has developed a very complete quantum-mechanical treatment of the phase angle problem for ν near ν_K. He has made use of his theory to predict the structure factors of Fe, Mo, and W. Hönl shows that his numerical values agree fairly well with certain experimental results.

In addition to the above-mentioned scattering problems from free atoms, we encounter other factors when we go to the crystalline state. As the atoms forming crystals are crowded together. the form of the potential barrier[3] of the atom is changed. The outermost conduction electrons are free to move in a periodic field. The effect of the conduction electrons has been discussed by Zener[4] and Scharwächter,[5] but both theory and experiment indicate that any effect on the f values is negligible at values of $(\sin \frac{1}{2}\phi)/\lambda$ greater than about 0.2. The motions of the next layer of electrons are less profoundly affected by the interatomic spacing, but they do move in orbits which are probably affected by the anisotropy of

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[1] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928).
[2] H. Hönl, Ann. d. Physik **18**, 625 (1933).
[3] J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934).
[4] C. Zener, Phys. Rev. **48**, 573 (1935).
[5] W. Scharwächter, Physik. Zeits. **38**, 165 (1937).

the crystal. We now have a picture of the crystal composed of a relatively few conduction electrons wandering to and fro in a rather free manner and of atoms whose scattering power has been made anisotropic.

We must now modify the whole picture by considering the thermal vibrations of the atoms. The effect of temperature on the scattering power of the atoms in a crystal has had several theoretical treatments[6] for the case of isotropic crystals. Zener[7] has made a theoretical study of the thermal vibrations in anisotropic crystals. For the cases of both isotropic and anisotropic crystals, it is assumed that each atom vibrates as a whole in the crystal lattice. A truer picture may be that the amplitude of vibration is different for the inner electrons than for the outer electrons—some distortion of the outer electron atmosphere being perhaps due to the thermal vibrations. However, in this paper we shall separate the thermal vibrations from the distortion of the outer electron atmosphere.

2. THE ATOMIC STRUCTURE FACTOR

Hönl's method of attacking the problem of the scattering power of an atom in the region of anamolous dispersion was first suggested by Waller,[8] who used a formula involving induced dipoles, quadrupoles, and octopoles in an atom which was under the influence of an electromagnetic wave. Hönl succeeded in developing the solution into a rapidly converging series by the use of spherical harmonics. The fact that Hönl did not include in his calculations the effect of spin or relativity is of no consequence in this paper since $h\nu_K$ for zinc is less than mc^2 by a factor of 50. The structure factor obtained by Hönl differs from the Hartree f by

$$\Delta f = -\xi_1^{(0)} - \frac{1}{2}\,\frac{\eta_1^{(0)}}{f+\xi_1^{(0)}} + \text{quadrupole terms}, \qquad (1)$$

where, according to Hönl's notation,

$$\xi_1^{(0)} = (2^7 e^{-4}/9)(4Q_2' - Q_3'), \qquad (2)$$

$$Q_n' = -\frac{x^2}{(1-\delta)^2}\int_x^\infty \left(\frac{1}{\zeta-1}+\frac{1}{\zeta+1}\right) d\zeta, \qquad (3)$$

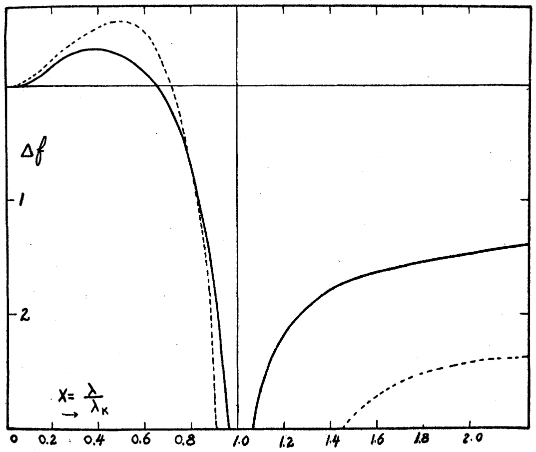

FIG. 1. The solid curve is the approximate Δf for zinc. It is assumed that other terms in (1) than the first are insignificant. The dotted curve is the classical theory.

$$\delta = \frac{(z-s)^2 - h\nu_K/Rhc}{(z-s)^2}, \qquad (4)$$

$$x = \lambda/\lambda_K, \qquad (5)$$

and s is the screening constant for the K shell. A table of values of δ is given elsewhere.[9] These values indicate a slowly varying function of the atomic number with the value of δ for zinc being 0.205.

On integration, (3) gives

$$Q_2' = \frac{x^2}{(1-\delta)^2}\log\left|1-\frac{1}{x^2}\right| \qquad (3a)$$

and $$Q_3' = \left(2x^2 + x^3\log\left|\frac{1-x}{1+x}\right|\right)\Big/(1-\delta)^3. \qquad (3b)$$

If only the $\xi_1^{(0)}$ term is considered, (1) becomes

$$\Delta f = 0.26\left\{\frac{4x^2}{(1-\delta)^2}\log\left|1-\frac{1}{x^2}\right| - \frac{2x^2}{(1-\delta)^3} - \frac{x^3}{(1-\delta)^3}\log\left|\frac{1-x}{1+x}\right|\right\}. \qquad (1a)$$

This formula can be used for calculating Δf for any atom and any wave-length and should be of use to other physicists when they are comparing experimental results with theory.

The solid curve of Fig. 1 is the graph of $\xi_1^{(0)}$ *vs.* x for zinc. In this simplification of Δf the wave mechanical picture differs from the clas-

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[6] See C. Zener and G. E. M. Jauncey, Phys. Rev. **49**, 17 (1936).

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

[8] I. Waller, Zeits. f. Physik **51**, 213 (1928).

[9] H. Hönl, Zeits. f. Physik **84**, 1 (1933).

sical picture principally because of the fact that wave mechanics considers the scattering power of the K electrons to be a function of the atomic number. For instance, in zinc the effective strength of the K shell is 1.31[9] rather than the classical value of 2. The broken curve shows the relation between $\xi_1{}^{(0)}$ and x for zinc on the Kramers-Kallmann-Mark theory.[10]

The second and third terms in (1) involve functions of $(\sin \frac{1}{2}\phi)/\lambda$. In the second term

$$\eta_1{}^{(0)} = -\pi\frac{2^7e^{-4}}{9}\left(\frac{4x^2}{(1-\delta)^2}-\frac{x^3}{(1-\delta)^3}\right) \qquad (6)$$

and in reality depends upon the absorption coefficient of the scattering material. This means that while it may have an appreciable value on the short wave-length side of the absorption edge, its magnitude on the long wave-length side is insignificant. This explains why the second term has been omitted in comparison with experimental data. In the experiments on zinc the value of the second term is two percent of the first term.

The third term is a quadrupole term which would normally be significant in the L absorption edge problem. Its effect is very small in the case of the K region and for the element zinc.

Table I gives the values of $\xi_1{}^{(0)}$ and of $\eta_1{}^{(0)}$ for various values of x in the case of zinc.

There seems to be little data to test the angle-dependence part of Hönl's theory. Rusterholtz[11] gives an empirical formula which he obtained by using primary rays of Zn $K\alpha$ and a scatterer of copper. This made $x=\lambda/\lambda_K=1.038$. His formula came out to be

$$\Delta f = 3.68 - 0.03(\sin \tfrac{1}{2}\phi)/\lambda.$$

The Hönl formula for these conditions is

$$\Delta f = 3.50 - \frac{0.025}{f-3.50} + 0.016\frac{2\cos^2\phi}{1+\cos^2\phi}.$$

Numerically these two formulas agree pretty well over the experimental range. It is noted that the quadrupole term is included. In this case the quadrupole term is of some importance because of the closeness of x to unity.

3. Powdered Crystal Structure Factors

Structure factors for powdered zinc have been obtained for Cu $K\alpha$-rays ($\lambda=1.54$A) by Brindley[12] and by Wollan and Harvey[13] and for Mo $K\alpha$-rays ($\lambda=0.71$A) by Miller.[14] These experiments give F values rather than f values. The true atomic structure factors, f, are obtained from the experimental F values by means of

$$f = Fe^M. \qquad (7)$$

In each experiment the front face method was used and the powder was obtained by sublimation.[12, 15]

If we call $f_{0.71}$ the structure factor of zinc for $\lambda=0.71$A and $f_{1.54}$ the structure factor for $\lambda=1.54$A and if we define $\Delta f'$ by

$$\Delta f' = f_{0.71} - f_{1.54}, \qquad (8)$$

then

$$\Delta f' = \Delta f_{0.71} - \Delta f_{1.54}, \qquad (9)$$

where Δf_λ is obtained from (1) or (1a) for $x=\lambda/\lambda_K$. For a given reflection e^M is the same regardless of the wave-length and hence by (7) and (9)

$$\Delta f' = (F_{0.71} - F_{1.54})e^M. \qquad (10)$$

Values of F are listed in Table II. The values shown in column 4 are the averages of Brindley's and of Wollan and Harvey's values for $\lambda=1.54$. Column 5 shows Miller's values for $\lambda=0.71$.

Table I. *Values of* $\xi_1{}^{(0)}$ *and* $\eta_1{}^{(0)}$ *for various values of* x *in the case of zinc.*

x	0.2	0.4	0.6	0.8	0.9	1.1	1.2	1.4	1.6	1.8	2.0
$\xi_1{}^{(0)}$	0.164	0.301	0.125	−0.692	−1.72	−2.66	−2.17	−1.78	−1.61	−1.53	−1.46
$\eta_1{}^{(0)}$	−0.206	−0.726	−1.52	−2.49	−3.01						

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[10] See A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment*, p. 292.

[11] A. A. Rusterholtz, Zeits. f. Physik **82**, 538 (1933).

[12] G. W. Brindley, Phil. Mag. **21**, 790 (1936).

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

[14] R. D. Miller, Phys. Rev. **51**, 959 (1937).

[15] W. A. Bruce, Rev. Sci. Inst. **8**, 451 (1937).

TABLE II. *Values of F.*

1 LINE	2 ψ	3 e^M	4 $F_{1.54}$	5 $F_{0.71}$	6 $f_{0.44}$	7 $F_{1.54}e^M$	8 $\Delta f'$ $\begin{pmatrix}\lambda=1.54\\ \lambda=0.44\end{pmatrix}$	9 $\Delta f'$ $\begin{pmatrix}\lambda=1.54\\ \lambda=0.71\end{pmatrix}$	10 $\Delta f_{H'}$
0002	0	1.10	19.7	22.3	23.7	21.7	2.0	2.86	2.43
$10\bar{1}0$	90	1.03	22.7	24.2	25.2	23.4	1.8	1.55	2.44
$10\bar{1}1$	65.0	1.06	19.3	22.0	23.9	20.4	3.5	2.86	2.44
$10\bar{1}2$	47.0	1.14	16.7	18.7	21.2	19.0	2.2	2.28	2.44
$10\bar{1}3$	35.6	1.20	13.7	15.9	18.7	16.4	2.3	2.64	2.45
$10\bar{2}0$	90.0								
$11\bar{2}2$	61.7	1.21	12.0	13.9	17.1	14.5	2.6	2.30	2.45
$20\bar{2}1$	76.9	1.17	12.4	13.9	16.7	14.5	2.2	2.75	2.45
$20\bar{2}3$	55.0	1.42	8.1	10.2	14.7	11.5	3.2	2.98	2.45
$10\bar{1}5$	23.2	1.69	6.7	8.2	13.7	11.3	2.4	2.54	2.46
$11\bar{2}4$	42.8								
$21\bar{3}1$	80	1.29	7.7	9.7	13.2	9.94	3.2	2.58	2.47
0006	0	1.49	6.3	7.8	12.3	9.4	2.9	2.24	2.47
$21\bar{3}2$	70.6								

4. TEMPERATURE FACTOR AND STRUCTURE FACTOR FROM DIFFUSE SCATTERING

From the theory of diffuse scattering from single crystals of zinc[16, 17] we have

$$S=S_{\mathrm{coh}}+S_{\mathrm{inc}}/(1+\alpha \text{ vers } \phi)^3, \tag{11}$$

where

$$S_{\mathrm{coh}}=f^2(1-e^{-2M})/Z \tag{12}$$

and

$$S_{\mathrm{inc}}=1-\Sigma E_r^2/Z. \tag{13}$$

In diffuse scattering experiments the intensities involved are so small that it has been found advantageous to use the continuous spectrum, and so the equation[17]

$$\left(\frac{S\rho}{\mu}\right)_{\mathrm{exp}}=\int(S_{\mathrm{coh}}+S_{\mathrm{inc}})\frac{\rho}{\mu}Id\lambda \tag{14}$$

has been developed. In this, $I(\lambda)$ is the distribution of the energy in the continuous spectrum. The integral involving S_{inc} can be calculated and (14) then is reducible to the form

$$\bar{G}(t)=\int G(t/\lambda)I(\lambda)d\lambda, \tag{15}$$

where $t=(\sin \frac{1}{2}\phi)$, and $G(t)$ and $I(\lambda)$ are experimental quantities. By a transformation of variables, this takes the form

$$h(t)=\int g(s)I(t,s)ds, \tag{16}$$

where $h(t)$ is a known function of t (an experimental curve) and $I(\lambda)$ is a known function of λ (also an experimental curve). Eq. (16) is an integral equation of the first kind.[18] This equation possesses a unique solution for our experimental conditions but there is no standard procedure for obtaining the solution. However, a graphic solution has been obtained and is explained in detail elsewhere.[17] By means of this graphic solution values of f and M have been obtained. These values of f are shown in column 6 of Table II. These f values are assigned to an average wave-length of 0.44A.

At a given temperature the temperature factor depends only upon the angle of orientation ψ and the scattering angle ϕ, and the formula for M at $T=295°$K is given by the empirical relation

$$M=(2.34\cos^2\psi+0.68\sin^2\psi)(\sin^2\tfrac{1}{2}\phi)/\lambda^2, \tag{17}$$

in which the constants of the equation are those found by Jauncey and Bruce.[17] The trigonometrical functions of the orientation angle are those given by Zener's theory.[7] The temperature factors obtained by use of (7) and the orientation angles in column 2 are listed in column 3.

There are several advantages in the diffuse scattering method, despite the low intensity and the tedious mathematics. In a soft metal like zinc where it is possible for small particles to be strained by van der Waals forces, it is very good to be able to use large single crystals that can be annealed, after they are grown and polished, and thus made entirely strain free.

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[16] G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **50**, 408 (1936).

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

[18] See R. Courant and D. Hilbert, *Methoden der Mathematischen Physik*, p. 97.

5. Results and Comparison with Theory

The f values for $\lambda=1.54\text{A}$ are shown in column 7 of Table II. These are obtained from the F values by multiplying the corresponding values shown in columns 3 and 4. Column 8 shows experimental values of $f_{0.44}-f_{1.54}$. Experimental values of $f_{0.71}-f_{1.54}$ are shown in column 9. The theoretical values of $f_{0.71}-f_{1.54}$ are shown in column 10. For these it is necessary to include the $\eta_1^{(0)}$ term and there is a slight dependence on angle. However, the variation is smaller than the experimental error and so the average of the values shown in column 9 is compared with that of column 10 thus

$$\left.\begin{array}{l}\Delta f'_{\text{exp}}=2.40\\ \Delta f'_{\text{theo}}=2.45\end{array}\right]0.71\text{A to }1.54\text{A.}$$

The theoretical value of $f_{0.44}-f_{1.54}$ is 2.45 and is practically constant with the angle. A comparison with the experiment is shown thus

$$\left.\begin{array}{l}\Delta f'_{\text{exp}}=2.57\\ \Delta f'_{\text{theo}}=2.49\end{array}\right]0.44\text{A to }1.54\text{A.}$$

This is a clear verification of the validity of Hönl's theory. It also gives one considerable faith in the f values of zinc as given by these four experiments and in the M values as given by Jauncey and Bruce. Table III lists the average of the experimental f values of the four experiments corrected for the change in structure factor due to the nearness of the K absorption edge.

Table III. *Structure factors for zinc.*

$(\sin\frac{1}{2}\phi)/\lambda$	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
f for $\psi=0°$	27.0	23.5	20.2	17.0	14.4	12.5	9.5	7.3
f for $\psi=90°$	28.4	25.9	21.5	18.2	14.9			

It is interesting to note that the f values for $(\sin\frac{1}{2}\phi)/\lambda=0.2$ for $\psi=0°$ and $90°$ differ by 2.4 electrons which is greater than 2. By reference to James and Brindley's paper[19] on the calculation of quantum-mechanical f values, it is seen that at this value of $(\sin\frac{1}{2}\phi)/\lambda$ the scattering for the two valence electrons is negligibly small, and so this variation of 2.4 electrons cannot be due to the valence electrons as stated in a previous paper.[17] The electron asymmetry thus extends deeper into the atom than the valence electrons.

The author wishes to thank Professor G. E. M. Jauncey for his encouragement and guidance in this work.

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[19] James and Brindley, Phil. Mag. **7**, 81 (1931).

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The Band Spectra of SrCl and SrH

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The spectra of SrCl and SrH are observed in absorption. The SrCl analysis given by Parker is confirmed. Measurement of the relative intensities of corresponding bands of the electronic doublet $^2\Pi\rightarrow{}^2\Sigma$ indicates that $^2\Sigma$ is the ground state. Rotational analyses of several bands of the C and D systems of SrH lead to values of B_e of 4.008 and 1.925 for the C and D states, respectively. Vibrational analyses of the two systems give $\omega_e=1206.2$, $x_e\omega_e=17.0$ for the $X\,^2\Sigma$ state; $\omega_e=1347$, $x_e\omega_e=23.5$ for the $C\,^2\Sigma$ state and $\omega_e=1014.1$ and $x_e\omega_e=15.4$ for the $D\,^2\Sigma$ state. The perturbations in the C and D states are discussed in terms of the interactions of the C, D, and E states.

Introduction

A total of five band systems of the SrH molecule have been reported in a series of papers by Watson and Fredrickson[1–4] and their co-workers. All but one of these systems have a strong (0,0) band, together with a weak (0,1)

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[1] W. W. Watson and W. R. Fredrickson, Phys. Rev. **39**, 765 (1932).

[2] W. R. Fredrickson, M. E. Hogan, Jr. and W. W. Watson, Phys. Rev. **48**, 602 (1935).

[3] W. W. Watson, W. R. Fredrickson and M. E. Hogan, Jr., Phys. Rev. **49**, 150 (1936).

[4] R. F. Humphreys and W. R. Fredrickson, Phys. Rev. **50**, 542 (1936).