SEPTEMBER 1, 1937 PHYSICAL REVIEW VOLUME 52

Experiments on the Variation of the Atomic Structure Factor of Nickel with X-Ray Wave-Length

WILLIAM P. JESSE
University of Chicago, Chicago, Illinois

(Received July 10, 1937)

X-ray measurements have been made with a vacuum ionization spectrometer on powdered nickel to determine the variation of the atomic structure factor in the region of the K absorption edge, $\lambda = 1.4839$A, and as far out as possible on the long wave-length side. Powdered NaCl and LiF have been used as comparison substances. Extensive measurements over a range of wave-lengths from 0.560 to 2.74A have been made. *Conclusions:* The experimentally determined dispersion curve for the atomic structure factor of nickel, based upon the difference between measured structure factor values on the long and short wave-length side of the K absorption edge, does not agree in shape with the theoretical curve of Hönl. The experimental curve rises more rapidly from the absorption edge and is then flatter than the theoretical curve. The two curves come into closer agreement at longer wave-lengths. The maximum discrepancy between theory and experiment is about 0.9 electron at $\lambda/\lambda_K = 1.11$. The predicted invariance of the structure factor decrement due to K electrons with $(\sin\theta)/\lambda$ is again confirmed.

INTRODUCTION

IN a previous paper,[1] experiments have been described in which the crystal structure factor in powdered KF was measured for wave-lengths in the neighborhood of the potassium K absorption edge. Such experiments showed the expected decrease in the crystal structure factor near the absorption edge on the short wave-length side and the change with wave-length was very closely in accord with the wave mechanical theory of Hönl. On the long wave-length side, however, the experimental values rose in a curve both steeper and higher than the theoretical curve and the *differences* in experimental values between the short and long wave-length sides were considerably less than the theory demands. Since it was impossible because of the limitations of the apparatus to carry the measurements as far as was desirable on the long wave-length side and thus determine the final shape of the experimental curve, it has seemed worth while to carry out further measurements on an element having a K critical absorption frequency within the range of convenient wave-lengths. For such measurements metallic nickel seemed well suited.

EXPERIMENTAL TECHNIQUE

The apparatus used in these experiments was the vacuum ionization spectrometer designed by Professor Allison and used by us in our previous measurements. Since the apparatus and the technique of measurement have been fully described in our previous paper,[1] any detailed account would seem unnecessary here. The powdered nickel used was chemically prepared by the reduction of nickel formate in hydrogen. The standard comparison substance was sodium chloride which was precipitated in a very fine powder by the addition of excess ethyl alcohol to a saturated aqueous solution of the salt. The resulting powder was dried, heated to 200°C, cooled and sifted through a bolting cloth having 275 meshes per inch. For the longer wave-lengths the standard substance was lithium fluoride. This was obtained from a chemical supply house and, according to the special analysis given on the container, showed negligible quantities of impurities. The LiF was also sifted through the bolting cloth. Throughout the experiment, the NaCl(200) plane was used as a standard comparison plane and for the longer wave-lengths the LiF(111) plane was used as a secondary standard. The latter was calibrated against NaCl(200) for the wave-lengths Cu $K\alpha$ and Fe $K\alpha$ so that the whole experiment is fundamentally based upon the value of the crystal structure factor for NaCl(200). Three separate briquets of powdered nickel and three briquets of NaCl were used during the course of the experi-

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

ment. The results from the different samples were very consistent.

The comparison of the relative power diffracted in the Debye-Scherrer ring from any given nickel plane to that diffracted from the standard plane was made by the second experimental method given in our paper. In this method the ionization chamber was moved in small steps, 5 or 10 minutes of arc, through the region of the diffracted beam and adjacent to it, until a level background was obtained. With Pliotron readings as ordinates and angles as abscissae, a smooth curve was drawn through the points obtained. The area under the peak and above the base-line is proportional to the diffracted power whose measurement is desired.

Experimental Results

From the measurement of the relative diffracted power from two planes either in the same crystal or in two different crystals the relative values of the crystal structure factor may be computed from the expression[2]

$$\frac{F_1}{F_2}=\frac{M_2}{M_1}\left\{\frac{j_2\mu_1\sin\theta_1}{j_1\mu_2\sin\theta_2}\left(\frac{1+\cos^2 2\theta_1}{\sin 2\theta_1}\right)^{-1}\times\left(\frac{1+\cos^2 2\theta_2}{\sin 2\theta_2}\right)\frac{[P_d]_1}{[P_d]_2}\right\}^{\frac{1}{2}},$$

where the subscripts refer to the individual planes.

F is the crystal structure factor.
M is the number of unit cells per unit volume.
j is the factor giving the number of possible orientations of the cell contributing to the diffraction halo in question.
μ is the linear absorption coefficient of the particles composing the briquet.
2θ is the angle between the forward directions of the incident and diffracted beams.

TABLE I. *Observed crystal structure factors, uncorrected for temperature. Based on* $\frac{1}{4}F[NaCl(220)]=15.62$ *for* $\lambda=0.709A$.

Powders	λ (A)	Line	Orders	θ's	Φ (θ)	j's	μ's	$P_{d_1}:P_{d_2}$	Value for Basic Plane	Result
Ni : NaCl	0.5598	Ag $K\alpha$	220 : 220	13°-00′ : 8°-05′	36.7 : 98.2	12 : 12	220 : 9.20	0.170	15.58	$f_{\mathrm{Ni}220}=12.85$
"	0.7092	Mo $K\alpha$	220 : 220	16°-34′ : 10°-16′	21.8 : 60.1	12 : 12	428 : 18.05	0.168	15.62	$f_{\mathrm{Ni}220}=12.75$
"	0.7092	Mo $K\alpha$	111 : 220	10°-03′ : 10°-16′	62.8 : 60.1	8 : 12	428 : 18.05	0.656	15.62	$f_{\mathrm{Ni}111}=18.02$
"	0.7092	Mo $K\alpha$	200 : 220	11°-38′ : 10°-16′	46.3 : 60.1	6 : 12	428 : 18.05	0.333	15.62	$f_{\mathrm{Ni}200}=17.24$
"	0.7857	Zr $K\alpha$	111 : 220	11°-09′ : 11°-23′	50.6 : 48.3	8 : 12	548 : 23.8	0.669	15.62	$f_{\mathrm{Ni}111}=17.93$
"	1.497	Ni $K\beta$	111 : 220	21°-37′ : 22°-06′	12.13 : 11.55	8 : 12	361 : 150	3.17	15.84	$f_{\mathrm{Ni}111}=12.66$
"	1.538	Cu $K\alpha$	200 : 220	25°-57′ : 22°-45′	8.02 : 10.81	6 : 12	427 : 163	1.69	15.84	$f_{\mathrm{Ni}200}=13.35$
"	1.656	Ni $K\alpha$	200 : 220	28°-05′ : 24°-35′	6.70 : 9.07	6 : 12	522 : 200	2.05	15.84	$f_{\mathrm{Ni}200}=14.71$
"	1.656	Ni $K\alpha$	111 : 220	24°-03′ : 24°-35′	9.54 : 9.07	8 : 12	522 : 200	4.80	15.84	$f_{\mathrm{Ni}111}=16.36$
"	1.656	Ni $K\alpha$	220 : 220	41°-44′ : 24°-35′	3.06 : 9.07	12 : 12	522 : 200	1.098	15.84	$f_{\mathrm{Ni}220}=11.26$
"	1.934	Fe $K\alpha$	220 : 220	51°-02′ : 29°-05′	2.75 : 6.19	12 : 12	795 : 312	1.47	15.91	$f_{\mathrm{Ni}220}=11.27$
LiF : NaCl	1.934	Fe $K\alpha$	111 : 220	24°-41′ : 29°-05′	8.99 : 6.19	8 : 12	69.4 : 312	2.69	15.91	$\frac{1}{4}F[\mathrm{LiF}(111)]=4.53$
"	1.538	Cu $K\alpha$	111 : 220	19°-25′ : 22°-45′	15.41 : 10.81	8 : 12	33.8 : 162.6	2.97	15.84	$\frac{1}{4}F[\mathrm{LiF}(111)]=4.62$
"	1.538	Cu $K\alpha$	200 : 220	22°-34′ : 22°-45′	11.01 : 10.81	6 : 12	33.8 : 162.6	3.52	15.84	$\frac{1}{4}F[\mathrm{LiF}(200)]=6.86$
Ni : LiF	2.744	Ti $K\alpha$	200 : 111	51°-15′ : 36°-21′	2.75 : 3.85	6 : 8	2054 : 187.3	1.07	4.65	$f_{\mathrm{Ni}200}=14.70$
"	3.353	Ca $K\alpha$	111 : 111	55°-38′ : 46°-24′	2.94 : 2.77	8 : 8	3445 : 339	2.56	4.69	$f_{\mathrm{Ni}111}=15.69$
							(sin θ)/λ			
Ni	0.7857	Zr $K\alpha$	200 : 111	12°-54′ : 11°-09′	37.25 : 50.61	6 : 8	.284 : .246	0.494	17.93	$f_{\mathrm{Ni}200}=16.97$
"	1.497	Ni $K\beta$	200 : 111	25°-11′ : 21°-37′	8.584 : 12.13	6 : 8	.284 : .246	0.437	12.66	$f_{\mathrm{Ni}200}=11.49$
"	1.497	Ni $K\beta$	220 : 111	37°-00′ : 21°-37′	3.719 : 12.13	12 : 8	.402 : .246	0.186	12.66	$f_{\mathrm{Ni}220}=8.05$
"	1.538	Cu $K\alpha$	111 : 200	22°-16′ : 25°-57′	11.38 : 8.02	8 : 6	.246 : .284	2.25	13.35	$f_{\mathrm{Ni}111}=14.57$
"	1.538	Cu $K\alpha$	220 : 200	38°-13′ : 25°-57′	3.51 : 8.02	12 : 6	.402 : .284	0.478	13.35	$f_{\mathrm{Ni}220}=9.87$
"	1.656	Ni $K\alpha$	111 : 200	24°-03′ : 28°-05′	9.54 : 6.70	8 : 6	.246 : .284	2.31	14.71	$f_{\mathrm{Ni}111}=16.26$
"	1.656	Ni $K\alpha$	220 : 200	41°-44′ : 28°-05′	3.06 : 6.70	12 : 6	.402 : .284	0.508	14.71	$f_{\mathrm{Ni}220}=10.98$
"	1.656	Ni $K\alpha$	220 : 111	41°-44′ : 24°-03′	3.06 : 9.54	12 : 8	.402 : .246	0.232	16.25	$f_{\mathrm{Ni}220}=11.24$
"	1.934	Fe$K\alpha$	200 : 220	33°-21′ : 51°-02′	4.58 : 2.75	6 : 12	.284 : .402	1.52	11.27	$f_{\mathrm{Ni}200}=15.21$
"	1.934	Fe $K\alpha$	111 : 220	28°-26′ : 51°-02′	6.51 : 2.75	8 : 12	.246 : .402	3.29	11.27	$f_{\mathrm{Ni}111}=16.25$
"	2.744	Ti $K\alpha$	111 : 200	42°-29′ : 51°-15′	3.00 : 2.75	8 : 6	.246 : .284	1.78	14.70	$f_{\mathrm{Ni}111}=16.27$
LiF	1.538	Cu $K\alpha$	111 : 200	19°-25′ : 22°-34′	15.41 : 11.01	8 : 6	.216 : .249	0.826	6.86	$\frac{1}{4}F[\mathrm{LiF}(111)]=4.56$

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[2] Compton and Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand), p. 419.

P_d is the power in the arc of the diffraction halo entering the ionization chamber window.

The experimental results are given in some detail in Table I, and in the various columns are found the quantities which appear in the above equation. The symbol $\Phi(\theta)$ represents a grouping of the trigonometric factors and is given by

$$\Phi(\theta)=(1+\cos^2 2\theta)/\sin^2\theta\cos\theta.$$

Since cubic crystals were used throughout, the values of M_2/M_1 were computed from the ratios of the cubes of the lengths of the sides of the unit cells. The cube edge of nickel was taken as 3.518*A* in this and other such computations.

As was stated before, the NaCl(220) plane was used throughout as a standard plane and the basic value for the crystal structure factor for $\frac{1}{4}F[\mathrm{NaCl}(220)]=f_{\mathrm{Na}}+f_{\mathrm{Cl}}$ was taken as 15.62, a value determined by James and Firth[3] for the wave-length 0.709*A*. Even though the wave-lengths used in the experiment are far removed from the *K* critical absorption wave-lengths of both sodium and chlorine, nevertheless the value for the structure factor for NaCl(220) is not entirely invariant and small corrections for dispersion must be made especially at the longer wave-lengths. These corrections, as before, were calculated from the theory of Hönl.[4] Tables of dispersion corrections for the atoms Na and F have been given in our previous paper. Since the chlorine atom is very close in atomic number to potassium, our previous calculations for the latter, with some extensions to the shorter wave-lengths, were considered a close enough approximation for the small corrections in question here. The values of $\frac{1}{4}F[\mathrm{NaCl}(220)]=15.62$ for $\lambda=0.709A$ plus the dispersion correction are found in vertical column 10 in the table. In this column are also found the values of $\frac{1}{4}F[\mathrm{LiF}(111)]$ based upon a value 4.56 for $\lambda=1.539$ and similarly corrected for dispersion whenever used as a secondary standard. In the latter part of Table I where comparisons between two nickel planes are given, the comparison value given in column 10 always by convention refers to the plane indexed in the denominator of the ratio in column 4. The last vertical column gives the final result for the atomic structure factors at room temperature derived from the comparisons indicated. This final value may often be the mean of from six to eight separate runs.

It is believed that the random error of measurement for lines Cu $K\alpha$, Ni $K\alpha$, and Fe $K\alpha$ represents a deviation from the above structure factor values of not more than 1 percent. The measurements with Ti $K\alpha$ are almost as good. On the short wave-length side the experimental conditions are not so favorable, and the error may be two or three times the above value. Systematic errors, which are by far the more important, will be discussed later. A difficulty was found in the measurement of Ni(200) with Mo $K\alpha$ in that the Ni(111) and Ni(200) peaks just failed to be resolved and a very small extrapolation at the foot of each curve was necessary. Different methods of making this extrapolation showed a negligible difference for the larger peak Ni(111) but did affect the smaller Ni(200) by several percent. The value of Ni(200) for Mo $K\alpha$ is, therefore, probably not quite so reliable as the other values obtained but is has been included for the sake of completeness. It gives throughout the experiment uniformly higher results than the others.

It should perhaps be noted at this point that the value here determined of $\frac{1}{4}F[\mathrm{LiF}(111)]=4.56$ for $\lambda=1.538A$ is about 10 percent lower than the one previously determined by us where a value 5.00 was obtained from a comparison of LiF(111) and NaCl(200) with wave-length 1.934*A*. The reason for this discrepancy is not entirely clear since the same LiF powder was used in both cases. The most probable reason would seem to be that for the NaCl(200) plane in the ground sodium chloride briquet formerly used a certain extinction error[5] was present, which has been here avoided by the use of finely precipitated powder and by taking a higher order plane as the standard plane. The present value of 4.56 for $\frac{1}{4}[\mathrm{LiF}(111)]$ is in good agreement with the experimental value 4.61 for $\lambda=0.709A$ of Havighurst,[6] and the value for $\frac{1}{4}F[\mathrm{LiF}(200)]$ of 6.86 agrees with his value of 6.72. The dispersion correction

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[3] James and Firth, Proc. Roy. Soc. **A117**, 62 (1927).

[4] Hönl, Zeits. f. Physik **84**, 1 (1933), Ann. d. Physik **18**, 625 (1933).

[5] As will be shown later, a systematic error of this type and magnitude in the standard NaCl (200) plane would cause but a very small change in the results previously obtained in potassium fluoride for the structure factor decrement, probably not more than the random experimental error.

[6] R. J. Havighurst, Phys. Rev. **28**, 869 (1926).

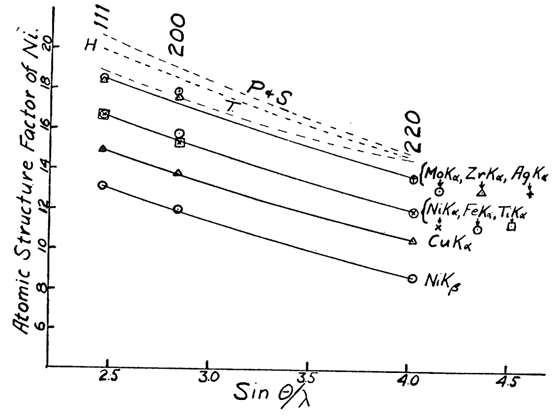

FIG. 1. Variation of the observed structure factor decrements with sin θ/λ.

is here negligible. Further when the present value for $\frac{1}{4}F[\text{LiF}(200)]$ is reduced to that corresponding to atoms at rest in the crystal by multiplication by a temperature factor $e^M=1.048$ for LiF(200) and a dispersion correction of 0.06 is subtracted, the final result 7.13 is comparable with and is but slightly lower than the sum of the theoretical Hartree values for f_{Li} and f_{F}; i.e., 7.30 for the corresponding value of $(\sin\theta)/\lambda$.

The final structure factor values in Table I, which are for nickel at room temperature, were reduced to corresponding values for atoms at rest in the lattice by means of the relation $f_0=fe^M$ where f_0 is the corrected structure factor and f is the factor observed at absolute temperature T. The value of M was determined by Waller's[7] formula

$$M=\frac{6h^2}{m_a k\Theta}\left(\frac{\Phi(x)}{x}+\frac{1}{4}\right)\frac{(\sin^2\theta)}{\lambda^2},$$

where h is Planck's constant,

m_a is the mass of the atom considered,
k is Boltzmann's constant,
x is the ratio Θ/T, where Θ is the characteristic temperature of the crystal.

The function $\Phi(x)$ is the result of the evaluation of a definite integral and is taken from a table of values given by Debye.[8] For nickel the characteristic temperature has been determined from thermal measurements by Lapp[9] who gives a value $\Theta=380°$. A check on this value was obtained by deriving the characteristic temperature for nickel from the known characteristic temperature for copper by comparison of the two crystals by the Lindemann[10] melting point formula. The value thus obtained was in excellent agreement with the value given above. In the first column of Table II are given final mean values of the structure factors derived from the comparisons indicated in Table I. The second vertical column shows the corresponding values of e^M and the third column gives the final values for the atomic structure factors corresponding to atoms at rest in the lattice. These values have been plotted against $(\sin\theta)/\lambda$ in Fig. 1. The legend to the right of the figure identifies the experimental points lying on each curve.

STATEMENT OF THEORY

The atomic structure factor is defined as the ratio of the amplitude of the wave scattered to a distant observing point P by an atom at 0 to the amplitude of the wave scattered to the same point P by a single electron replacing the atom, it being assumed that the electron scatters in the

TABLE II. *Temperature corrections applied to values of* f_{Ni} *of Table I.*

fNi Table I	e^M	$f_0=fe^M$	INDICES	λ (A)	LINE
18.02	1.025	18.47	(111)	0.7092	Mo $K\alpha$
17.93	"	18.38	(111)	0.7857	Zr $K\alpha$
12.66	"	12.98	(111)	1.497	Ni $K\beta$
14.57	"	14.93	(111)	1.538	Cu $K\alpha$
16.27	"	16.67	(111)	1.656	Ni $K\alpha$
16.25	"	16.65	(111)	1.934	Fe $K\alpha$
16.27	"	16.67	(111)	2.744	Ti $K\alpha$
15.69	"	16.08	(111)	3.353	Ca $K\alpha$
17.24	1.034	17.83	(200)	0.7092	Mo $K\alpha$
16.97	"	17.55	(200)	0.7857	Zr $K\alpha$
11.49	"	11.88	(200)	1.497	Ni $K\beta$
13.35	"	13.81	"	1.538	Cu $K\alpha$
14.81	"	15.32	"	1.656	Ni $K\alpha$
15.23	"	15.75	"	1.934	Fe $K\alpha$
14.70	"	15.22	"	2.744	Ti $K\alpha$
12.85	1.068	13.73	(220)	0.5598	Ag $K\alpha$
12.75	"	13.62	"	0.7092	Mo $K\alpha$
8.05	"	8.60	"	1.497	Ni $K\beta$
9.87	"	10.54	"	1.538	Cu $K\alpha$
11.19	"	11.95	"	1.656	Ni $K\alpha$
11.27	"	12.04	"	1.934	Fe $K\alpha$

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[7] I. Waller, Zeits. f. Physik **17**, 398 (1923); Diss. Uppsala (1925).

[8] P. Debye, see Compton and Allison, reference 2, p. 437.

[9] E. Lapp, Ann. de physique **12**, p. 442 (1929).

[10] Lindemann, Zeits. f. Electrochem. **17**, 817 (1911).

J. J. Thomson manner. So long as the frequency of the wave which is scattered remains far removed from any critical absorption frequency in the atom itself, the value of the structure factor changes but little with wave-length. When, however, frequencies only slightly higher than the K critical absorption frequency are used, then the amplitude of the two K electrons in the atom is greatly increased by resonance and a phase change also results. As a consequence, destructive interference is obtained between the radiation scattered by the K electrons and that scattered by the other electrons in the atom, and for frequencies very close to the critical absorption frequency the atomic structure factor may be greatly reduced. On the long wave-length side of the absorption edge the atomic structure factor rises again as we pass out of the region of resonance but never attains the full value experienced on the short wave-length side since the K electrons no longer share in the scattering process. The shape of the curves for the variation of the atomic structure factor with wave-length depends in a large measure upon the distribution with wave-length assumed for the virtual oscillators in the atom. The net difference between the values of the structure factor for $\lambda \to 0$ and $\lambda \to \infty$ gives the so called "oscillator strength"; i.e., the normal contribution of the electrons in the K shell to the scattering. Using the wave mechanics, Hönl[4] has been able to compute both the oscillator strength and the distribution of oscillators with wave-length from purely theoretical grounds. His equation for the expected change in the structure factor with wave-length is given by

$$\Delta f = -\frac{2^7 e^{-4}}{9}\left[\frac{4x^2 \ln|1-x^{-2}|}{(1-\Delta)^2} - \frac{1}{(1-\Delta)^3}\left\{x^3 \ln\left|\frac{1-x}{1+x}\right| + 2x^2\right\}\right]. \quad (1)$$

Here Δf, the so-called "structure factor decrement," is defined as $\Delta f = f_{\lambda\to 0} - f_\lambda$ where f_λ is the value of the structure factor for a wave-length λ and $f_{\lambda\to 0}$ the value for wave-lengths so short that all dispersion effects are negligible.

x represents the ratio λ/λ_K where λ_K is the wave-length value at the K critical absorption edge.
Δ is an atomic screening correction which in the case of nickel has the value 0.209.
e is the natural logarithm base.

For large values of x approaching infinity the above expression gives a value of $\Delta f = 1.32$ which is the oscillator strength of the K electrons of nickel. Hönl has further shown that the Δf values are independent of $(\sin\theta)/\lambda$, or rather that the variations are so small as to be undetectable experimentally except possibly for very heavy atoms.

TABLE III. *Determination of decrement Δf from corrected values in Table II.*

	λ(A)	Ni(111)	Ni(200)	Ni(220)	Ni(111)	Ni(200)	Ni(220)	MEAN Δf (Exp)	Δf HÖNL THEORY
$f_{\lambda\to 0}$		$f_{\text{Mo }K\alpha}-.28$ $=18.19$	$f_{\text{Mo }K\alpha}-.28$ $=17.55$	$f_{\text{Mo }K\alpha}-.28$ $=13.34$	$f_{\text{Zr }K\alpha}-.24$ $=18.14$	$f_{\text{Zr }K\alpha}-.24$ $=17.31$	$f_{\text{Ag }K\alpha}-.30$ $=13.43$		
$\Delta f_{\text{Ni }K\beta}$	1.497	5.21	5.67	4.74	5.16	5.43	4.83	5.17	5.00
$\Delta f_{\text{Cu }K\alpha}$	1.538	3.26	3.74	2.80	3.21	3.50	2.89	3.23	3.56
$\Delta f_{\text{Ni }K\alpha}$	1.656	1.52	2.23	1.39	1.47	1.99	1.49	1.68	2.55
$\Delta f_{\text{Fe }K\alpha}$	1.934	1.54	1.80	1.30	1.49	1.56	1.39	1.51	1.94
Exp. values below relative to mean $\Delta f_{\text{Ni }K\alpha} = 1.68$.									
$\Delta f_{\text{Ti }K\alpha}$	2.744	1.68	1.78					1.73	1.58
$\Delta f_{\text{Ca }K\alpha}$	3.353	2.27						2.27	1.45

COMPARISON OF THEORY AND EXPERIMENT

In Table II the third column gives the values of the atomic structure factors for nickel corrected for temperature. Fig. 1 gives a plot of these values against $(\sin \theta)/\lambda$ for the various wave-lengths used. The invariance predicted by the Hönl theory of the structure factor decrement with $(\sin \theta)/\lambda$ is clearly shown by the fact that the curves representing experimental results are all parallel. This has previously been shown to be the case by ourselves[1] and others. To determine values of Δf, which is defined as $f_{\lambda\to 0} - f_\lambda$, entirely by experiment would be quite impractical since it would involve the use of infinitely short waves with their attendant difficulties, both theoretical and practical. It is therefore assumed that the theoretical equation of Hönl gives the correct value of Δf for the wave-lengths corresponding to Ag $K\alpha$, Mo $K\alpha$ and Zr $K\alpha$. It is further assumed that such Δf values are included in the values for the atomic structure factors experimentally determined for all planes with these wave-lengths. Our former paper has shown excellent relative agreement over a wide range of wave-lengths between the Hönl theory and experiment on the short wave-length side of the absorption edge of the potassium atom and there seems to be no reason to believe that the small Δf's here assumed are greatly in error. Their values are -0.30, -0.28 and -0.24 electrons for wave-lengths corresponding to Ag $K\alpha$, Mo $K\alpha$ and Zr $K\alpha$, respectively. If such negative decrements are added respectively to the values in Table II of the structure factors for the various planes determined with these three wave-lengths, we obtain values of $f_{\lambda\to 0}(111)$, $f_{\lambda\to 0}(200)$, $f_{\lambda\to 0}(220)$, corresponding to each set of measurements. The values thus obtained are tabulated in the top horizontal row of Table III. By definition, therefore, we may compute the decrement Δf for any wave-length λ by subtracting the structure factor derived at such a wave-length from the corresponding $f_{\lambda\to 0}$. This subtraction has been carried out in the next four horizontal rows of Table III, the values from Table II being subtracted from the values in the top row. Each horizontal row thus tabulates for the given wave-length at the left the values of the decrement derived from different combinations of experimental values. The mean of these is given in the column next to the last, while the last column gives the theoretical value of Hönl derived from Eq. (1). For the values of the structure factors obtained with Ti $K\alpha$ and Ca $K\alpha$ a slightly different procedure was followed. Because of the longer wave-length involved, measurements of only two planes with Ti $K\alpha$ and one with Ca $K\alpha$ were possible. The structure factors (Table II) for such planes were compared with the corresponding values for Ni $K\alpha$ and the mean $\Delta f_{\mathrm{Ni}\ K\alpha} = 1.68$ was raised or lowered correspondingly. The values for the last two wave-lengths are thus relative to the value determined for Ni $K\alpha$. Because the value $\Delta f_{\mathrm{Ca}\ K\alpha}$ rests upon measurements of a single plane, Ni(111), as compared with measurements of three planes for most of the wave-lengths used, very little relative weight should be given to this single measurement. There may also be some uncertainty here as to the effect of the very high absorption coefficient, which is almost double that encountered in any previous work. No anomalous results, however, traceable to such a source have so far been observed.

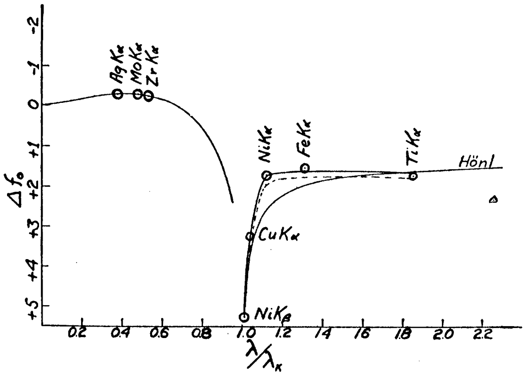

FIG. 2. The variation of the mean experimental decrement as a function of relative wave-length and comparison with Hönl theory. The point △ represents a determination for a single plane with line Ca $K\alpha$.

A comparison of the last two vertical columns of Table III and a reference to Fig. 2 where the results are plotted shows definite discrepancies between theory and experiment. The experimental curve rises much more rapidly than the theoretical curve on the long wave-length side and for the wave-length corresponding to Ni $K\alpha$ is almost 0.9 of an electron higher than the theoretical curve. Such an error, it is believed, is distinctly beyond the error of experiment. Since because of our method of fitting the curve on the short wave-length side, we are dealing only in differences between structure factors on the long and short wave-length sides of the absorption edge, the discrepancy could, of course, lie in incorrect predictions of the theory for the short wave-length values of Δf. Two arguments can be advanced against such a supposition. In our former paper we found that the shape of the theoretical curve on the short wave-length side was in excellent agreement with the actual experimental curve although a similar discrepancy was found for the differences between the two sides. Also here for nickel the different shapes of the experimental and theoretical curves on the long wave-length side preclude any possibility of bringing the curves into coincidence even though they are fitted to each other at any one given point on the long wave-length side. Fig. 1 shows that the structure factor values for Ni $K\alpha$, Fe $K\alpha$ and Ti $K\alpha$ are very nearly the same. Theory, however, demands a difference of almost 1 full electron between the values for Ni $K\alpha$ and Ti $K\alpha$ and 0.6 electron between the values for Ni $K\alpha$ and Fe $K\alpha$. Since these wave-lengths were especially favorable to accurate measurement, it is difficult to believe that such differences are attributable to experimental error. If we neglect the inconclusive point for Ca $K\alpha$ it would seem that theory and experiment are in better accord as we go to longer wave-lengths from the point for Ni $K\alpha$. Thus one would suspect that any inadequacy in the theory results from an improper estimate of the distribution of virtual oscillators with frequency rather than an erroneous determination of the oscillator strength.

Discussion of Results

Before comparing the above results with those of other experiments it might be well to emphasize the manner in which the experimental Δf is determined in this case. Here experimental values of f_0 have been determined for any given plane for wave-lengths on the long wave-length side of the limit and also for a standardizing wave-length on the short wave-length side. The experimental values are then fitted to the Hönl dispersion curve at the origin $\lambda_{\to 0}$ by applying to the value f_0 for the standardizing wave-length the dispersion value Δf calculated from Hönl's theory for this wave-length. The values of Δf obtained thereafter from the data are as nearly as possible the result of pure experiment and do not rely, as in some experiments, upon subtracting experimental values of f_0 determined on the long wave-length side from values of f_0 computed from theory. The advantage of the method here used is a very real one. Should the experimental values of f_0 contain errors which are not a function of wave-length, then the values of f_0 would be raised or lowered by the same percent on both sides of the limit and the Δf decrement determined would suffer the same percent error as the values of f_0. The method would thus minimize the effect of erroneous temperature corrections, incorrect values of M, the number of unit cells per unit volume, and primary extinction which, according to Darwin,[11] is a function of the order of the reflection rather than of the wave-length. On the other hand, the compensation would not be so good for systematic errors which are a function of wave-length. Thus errors in the linear absorption coefficient, for example, would not be well compensated for except in so far as they might result from erroneous densities. As an example of the above discussion, in Fig. 2 there is shown the resultant change in the experimental Δf's of assuming the determined structure factors to be uniformly 10 percent too low. If every experimental structure factor is raised then 10 percent, and hence every value of Δf by the same amount, the dotted curve in the figure shows the final result. As may be seen, such a curve differs from the original curve by hardly more than the random experimental error. If, on the other hand, the values on the long wave-length side had been formerly subtracted from an invariant value on the short wave-length side, let us say a theoretically derived value, then the ten percent increase might have introduced changes in Δf in some cases as large as the original values of Δf.

A resumé of previous work done on this problem has already been given[1] and a repetition of this would, therefore, seem unnecessary here. A mention, however, of the more recently determined values of Brindley and Spiers[12] seems de-

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[11] C. G. Darwin, Phil. Mag. **43**, 800 (1922).

[12] G. W. Brindley and F. W. Spiers, Phil. Mag. **20**, 865 (1935).

sirable and their values are given in Table IV for comparison with the present values. Brindley and Spiers made a comparison between powdered nickel and powdered KCl for the line Cu $K\alpha$, the standard values of the structure factors for KCl being those determined by James and Brindley[13] through comparison of single crystals of KCl and NaCl. It will be seen that the values for four planes for nickel are in excellent agreement with those of the present paper given in column 2. Later, however, in the light of comparisons with powdered aluminum as a standard substance, Brindley[14] has concluded that the James and Brindley values of KCl are incorrect and must be raised just 10 percent. The fourth column of Table IV gives his revised values for nickel based upon aluminum powder as a standard. The values used by Brindley for the atomic structure factors for aluminum were the theoretically derived ones of Hartree. The Hartree curve, atomic structure factor against $(\sin\theta)/\lambda$, was corrected to room temperature and a dispersion correction was added. To this was fitted at one point the similar experimental relative curve, i.e., atomic structure factor against $\sin\theta/\lambda$, through the multiplication of the latter by an arbitrary factor.

Although but little indication is given in the paper in regard to the difficulties with KCl, Brindley seems to assume that the differences obtained between his two comparison substances are the result of the fact that KCl is a poor standard substance. The comparison in Table IV might possibly indicate that the basic difficulty lies in an incorrect absolute value of the atomic structure factors for NaCl. As is shown in the table, the same result is apparently obtained for nickel powder whether we use powdered NaCl directly as a standard or KCl powder with structure factors determined through an original comparison with a single NaCl crystal. No value is given by James and Brindley[13] for the absolute value of the structure factor for the plane of NaCl in their paper on the comparison of KCl and NaCl but it is undoubtedly a value consistent with the value of NaCl by James and Firth used throughout the present work. A further interesting comparison may be made with the results shown in Table IV. If the values derived in the present paper are reduced to equivalent values referred to aluminum powder, then all values should be raised by 10 percent including the average values for $f_{\lambda\to 0}$. The mean values derived from the top row of Table III are re-tabulated in column 5 of Table IV. Column 6 shows them raised by 10 percent. Column 7 shows approximate Hartree $f_{\lambda\to 0}$ values for nickel which are given in Brindley's paper. In the absence of directly computed Hartree values for nickel an approximate curve is interpolated between the Thomas and the Pauling and Sherman curves, Fig. 1, in the same manner that the computed curve of Hartree for copper divides the interval between the corresponding two curves for copper. The Hartree curve, marked H in Fig. 1, while only approximate, is probably not greatly different from what would be computed directly by the Hartree method. The agreement between columns 6 and 7 would indicate a certain internal consistency in the results based on aluminum powder using theoretical Hartree values.

TABLE IV. *Comparison of present results with results of other experiments.*

Plane	f_0 Values for Cu $K\alpha$ W.P.J.	f_0 Values Cu $K\alpha$ KCl Stand. B&S	f_0 Values Al. Stand. Brindley Col. 3+10%	$f_{\lambda\to 0}$ Mean Values W.P.J.	$f_{\lambda\to 0}$ W.P.J. Al. Stand. Col. 5+10%	$f_{\lambda\to 0}$ Approx. Hartree Values	Δf Brindley Col. 7 −Col. 4	Δf W.P.J. Col. 5 −Col. 2
Ni(111)	14.93	15.3	16.83	18.17	20.00	19.9	3.07	3.24
Ni(200)	13.81	13.55	14.88	17.43	19.17	18.5	3.62	3.62
Ni(220)	10.54	10.45	11.49	13.38	14.72	14.7	3.21	2.84
Ni(311)	8.75	8.7	9.56			12.7	3.33	
Ni(331)			6.06			10.4	4.34	
					Mean		3.51	3.23

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[13] R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121**, 154 (1928).

[14] G W. Brindley, Phil. Mag. **21**, 778 (1936).

In this connection reference might be made to a table in a paper by Renninger[15] in which he compares the various experimental absolute determinations made for structure factors for the planes NaCl(200), NaCl(400), NaCl(600) and shows that differences amounting to more than 10 percent exist between the various determinations. His own determination obtained with a double crystal spectrometer for the line Cu $K\alpha$ is about 7 percent higher than the James and Firth value for NaCl(400) and Renninger's determination is more than 10 percent higher for NaCl(600). Thus there would seem to be possible grounds for questioning the correctness of the value 15.62 for $\frac{1}{4}F[\text{NaCl}(220)]$ as determined by James and Firth. However, it must be noted that the experimental value of $\frac{1}{4}F[\text{LiF}(200)]$ here obtained which is based upon the above value for NaCl(220) is quite consistent with the theoretical value of Hartree and the same applies to a lesser degree to the value of $\frac{1}{4}F[\text{LiF}(111)]$.

In the light of the above discussion it is possible that later work may show that the absolute value here used for $\frac{1}{4}F[\text{NaCl}(220)]$ is not correct but should be raised by 10 percent as might be indicated by Brindley's results with an aluminum standard. Even in such an event the final experimental values of Δf here given would be altered but little provided we assume that *any existing error is not a function of wave-length* as would very probably be the case. The Δf values in column 9, Table III, would then be increased by 10 percent. The dispersion curve resulting under these conditions is that given by the dotted line in Fig. 2 instead of the full line. As can be seen, the difference between the curves is very small. The experimental Δf is still definitely higher than the Hönl curve in the vicinity of the point for Ni $K\alpha$ The point corresponding to the line Cu $K\alpha$ is, however, now in almost exact agreement with the theory.

Brindley[14] has also determined in the same manner as for nickel the decrement Δf for metallic copper for the line Cu $K\alpha$ ($\lambda = 1.539$) and finds a value in very close agreement with the theoretical value of Hönl. Since in Eq. (1) the shielding constant Δ is a very slowly changing function of the atomic number, the predicted value of Δf varies but little for elements of adjacent atomic number for the same value $x = \lambda/\lambda_K$. The value determined by Brindley for metallic copper for Cu $K\alpha$ should thus be directly comparable with the present value for metallic nickel for Ni $K\alpha$ since the value of x is practically the same in the two cases. Here the two experiments are definitely in disagreement, his value of $\Delta f = 2.61$ being definitely lower than the value found here. On the other hand, Lameris and Prins[16] using the method of total reflection of the general x-radiation from a mirror of metallic nickel have obtained a dispersion curve which shows a steeper rise for the structure factor than the theory predicts on the long wave-length side of the limit, just as is indicated in the present experiments

Finally, the present experiments are in qualitative agreement with our previous results[1] for the potassium atom in KF in that in both cases the rise in the value of the atomic structure factor on the long wave-length side of the limit is more rapid and higher than the theory predicts. Quantitatively, however, the agreement is not so good since the differences between theoretical and experimental values of Δf are relatively less in the present experiments on nickel. The former results for potassium would indicate an erroneous value of the total oscillator strength for the K electrons of potassium from the Hönl theory as well as an erroneous distribution of virtual oscillators. The present results for nickel indicate a correct total oscillator strength but an incorrect distribution of virtual oscillators.

In conclusion, the author wishes to extend his thanks to the chairman of the department of physics, Dean Henry G. Gale, for the excellent facilities provided for this work. He wishes also to thank especially Professor S. K. Allison, who designed the vacuum ionization spectrometer used, and to whom he is indebted for many suggestions and for discussions of the present problem.

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[15] M. Renninger, Zeits. f. Krist. **89**, 373 (1934).

[16] A. J. Lameris and J. A. Prins, Physica **1**, 881 (1934).