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

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A vacuum ionization spectrometer has been constructed in which an externally controlled, motor-driven slide brings either of two powder specimens into the path of the primary x-ray beam. Comparison of the diffracted power in the Debye-Scherrer rings from NaCl, NaF, LiF, and KF powders have been made, with a FP-54 Pliotron circuit to detect the ionization currents. In the studies on KF a range of wave-lengths from 1.538A to 4.146A has been used. On the short wave-length side, the expected decrease of the crystal structure factor was observed in KF. Beyond the K edge of potassium, the crystal structure factor rose again, but considerably more than predicted. Conclusions: Hönl's computations based on the wave-mechanical theory of x-ray dispersion do not correctly give the observed structure factor differences for the (200) diffraction halo from powdered potassium fluoride on the long and short wave-length sides of the potassium K edge. The predicted invariance of the structure factor decrement due to K electrons with scattering angle for light elements is confirmed in our experiments.

INTRODUCTION

THE crystal structure factor F is defined by the relation

$$F=\sum_j f_j \exp\left[2\pi Ni(hx_j+ky_j+lz_j)\right], \qquad (1)$$

where the summation is to be carried out over all the atoms in the unit cell. f_j is the atomic structure factor of the atom j, whose coordinates in the unit cell are $x_jy_jz_j$. N is the order computed from a simple translatory lattice corresponding to the classification of the crystal under investigation and having one atom per unit cell. hkl are the Miller indices of the reflecting plane. Relative values of F may be obtained by comparing the powers of the diffracted Debye-Scherrer rings from powdered samples, provided suitable precautions are taken. If F is a known function of the f_j's, i.e., if the crystal structure is completely known, it is possible, for simple crystals, to compute f values of the constituents of the crystal from a sufficiently complete set of F values.

The object of the experiments reported here was to investigate the variation of f with λ in the region of the K critical absorption frequency. We chose to study a light atom, because if the total number of extranuclear electrons is small, the structure factor decrements due to the anomalous K electron behavior are a relatively larger fraction of the structure factor. Other considerations, such as the necessity of finding an atom having its K absorption edge very near the wave-length of a strong x-ray line led to the decision to study the behavior of the potassium atom in KF. The power diffracted from powdered KF was compared with that diffracted by NaF and LiF, which should show only very minute anomalous behavior in the region around the potassium K limit, and these in turn were calibrated against NaCl at wave-lengths far from

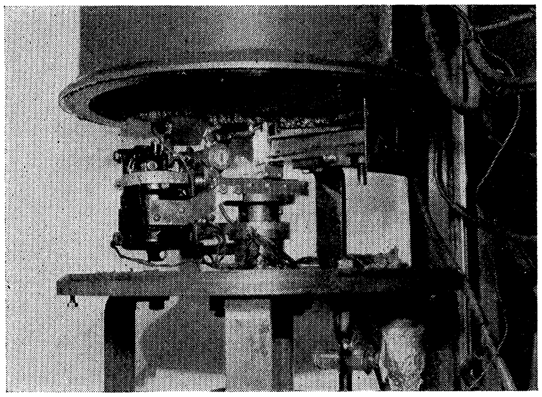

FIG. 1. Photograph of vacuum ionization spectrometer with the cover lifted.

the chlorine critical absorption edge. The potassium K absorption limit in KF has been measured at 3.4277A by Stelling,[1] and this is a different value than that observed in metallic potassium by Lindh[2] (3.4310). Wave-lengths in this region are so readily absorbed in air that a vacuum spectrometer is needed.

A. EXPERIMENTAL PART

The vacuum ionization spectrometer

The vacuum ionization spectrometer was similar to the vacuum double spectrometer designed and constructed in this laboratory, and used by Parratt.[3] Fig. 1 shows a photograph of the spectrometer with the lid raised. The metal x-ray tube, of the type designed in this laboratory by Dershem,[4] is attached to the raised cover, upon which are mounted the diffusion pumps used in its evacuation. Thus the vacuum in the instrument itself, which is merely the lowest pressure attainable from a Megavac pump, acts as a fore-vacuum for the exhaustion of the x-ray tube. At the right of Fig. 1 are seen the slits, which were carefully machined and ground steel bars, placed side by side, and actuated by a mechanism such that the distance between them may be changed, but they are constrained to move parallel to themselves. Another slow motion device turns the entire slit assembly about a vertical axis, so that the central ray may be made to pass through the axis of rotation of the sleeves carrying the powder frames and the ionization chamber.

At the left of Fig. 1 is seen an electric motor, with speed reduction gears built in, which moves the frame carrying the powders forward and backward, so that first one sample and then the other can be brought into the path of the x-ray beam. The position of the framework carrying the powders can be read through a glass window in the top of the lid, and settings can be repeated with ease to 0.0025 cm.

The front slit of the cylindrical ionization chamber can be seen in the central background. The chamber was filled with argon gas at one atmosphere. The outer wall of the chamber is charged to 90 volts; the insulated collecting electrode leaves the chamber at the rear, and the ionization current is conducted along insulated rods which enter the central shaft of the instrument and pass down the axis of rotation. Some of the ionization current readings were taken on a Cambridge Compton electrometer, later a FP-54 Pliotron amplifying circuit was installed.

The angular positions of the ionization chamber and powder frames can be changed by rotation of sleeves which extend down the central axis, and the rotations can be read to about 2 minutes of arc on a divided circular scale. A sine screw operating on the sleeve carrying the powder frames allows angular rotations of 30 seconds of arc to be easily made. Numerical data on the spectrometer are given in Table I.

TABLE I. *Dimensions of the vacuum ionization spectrometer.*

From x-ray tube target to central axis	27 cm
Length, height, width, of slits	15, 1.55, 0.041
From central axis to ionization chamber window	9.0
Diameter, length, of cylindrical ionization chamber	3.5, 6.5
Width, height, of ionization chamber slit	0.148, 1.0

Experimental technique

The substances which were used, namely, NaCl, NaF, LiF, and KF were obtained from various chemical supply houses which sell analyzed chemicals. All were stated to contain only

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[1] O. Stelling, Siegbahn, *Spektroskopie der Röntgenstrahlen* (J. Springer, Berlin, 1931), p. 290.

[2] A. E. Lindh, Siegbahn, *Spektroskopie der Röntgenstrahlen* (J. Springer, Berlin, 1931), p. 289.

[3] L. G. Parratt, Phys. Rev. **41**, 553 (1932).

[4] E. Dershem, Rev. Sci. Inst. **7**, 86 (1936).

traces of foreign substances. Because of the fact that the presence of chlorine as an impurity in the fluorides would have introduced serious error, tests for Cl were made on the actual samples used, insuring its absence in appreciable amounts. The powders were ground for several hours in a porcelain mortar, and in some cases finally in an agate mortar; then compressed into briquets in steel frames. These frames were rectangular pieces of steel 3 mm thick and 3.2×4.0 cm, with a rectangular aperture 1.6×2.3 cm to hold the powder. Enough powder was used so that after compression the aperture was over full. The face of the briquet from which diffraction was to occur was then eroded down to the level of the frame by rubbing on sandpaper. In this way we avoided using layers which had been immediately adjacent to a metal surface during compression and which might thus have been oriented. The normal way in which the powers diffracted into the (200), (220), and (222) rings from KF decreased, indicated lack of orientation, at least at 1.538A wave-length.

Potassium fluoride is hygroscopic, forming a hydrate, KF $2H_2O$, which melts at 41°C. Since the hydrate was supplied, dehydration was necessary. The hydrate was heated overnight on a steam-bath, thus removing all but traces of the water without danger of hydrolysis. The dried material was then heated to 600°C in a platinum crucible. The grinding operations were carried out in a mortar placed on an electric heater which maintained a temperature of over 100°C throughout the operation, and the compressing was done in a heated press. The KF was then stored in a desiccator over P_2O_5 pending use, and a large pan of P_2O_5 was always kept in the spectrometer. Air was admitted to the instrument through a drying train.

The Pliotron circuit[5] used in the latter stages of the experiment had a sensitivity of 4×10^{-16} amp. per mm scale deflection. The weakest powder lines, such as the diffraction of Ti $K\alpha$ in the order (222) from KF gave deflections of 1.0 cm above the background, with the x-ray tube running at 30 kv and 3 ma. Strong lines, like Cu $K\alpha$, from (200) NaF would have given 60 cm deflection at 30 kv and 10 ma if the sensitivity of the circuit had not been reduced. Thus the measured ionization currents varied from 4×10^{-15} to 2.4×10^{-13} amp.

In the theory of diffraction by a powder consisting of randomly oriented particles, one calculates the power diffracted into an arc of a Debye-Scherrer ring. Two experimental methods were used to measure relative values of this power.

(1) The ionization chamber was moved in angular steps equal to the angular width of its window through the region in which a diffracted maximum appeared. The background readings were determined at positions adjacent to the diffracted beam. The sum of the differences between the readings in the beam and the background readings is proportional to the power which it is desired to measure. The method is easily seen to be equivalent to using a single position of an ionization chamber with a slit wide enough to take in the entire beam of diffracted x-rays. The angular width of the ionization chamber window (40 min.) was measured by moving the chamber past the diffracted beam from a single calcite crystal, which diffracts a beam of the same angular divergence as that leaving the slits. For the powder specimen three or four adjacent positions were always sufficient to cover the diffracted beam.

(2) 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 power whose measurement is desired.

These two methods were compared many times and were shown to give the same power ratio for two diffraction rings. The technique of making a measurement was as follows: Let us suppose the relative powers of LiF (111) and KF (200) for a certain wave-length are required. The powder frame support is moved by means of the motor until LiF is in the x-ray beam. The sleeve carrying the powder frames is then rotated until the incident and diffracted beams enter and

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[5] L. A. DuBridge and H. Brown Rev. Sci. Inst. **4**, 532 (1933).

TABLE II. *Sets of readings to indicate the accuracy of repetition.* F values based on $\frac{1}{4}F_{\mathrm{NaCl}}(200)=20.80$, $\frac{1}{4}F_{\mathrm{NaF}}(200)=14.55$.

POWDERS	λ(A)	ORDERS	DATE	METHOD	$[P_d]_1/P_d]_2$	RESULT
LiF; NaCl	1.934	(111); (200)	Dec. 24, '35	2	1.66	$\frac{1}{4}F_{\mathrm{LiF}}(111)=$ 4.98
"	"	"	"	2	1.72	" 5.08
"	"	"	Jan. 25, '36	2*	1.63	" 4.94
						Average 5.00
KF; NaF	4.146	(200); (200)	Nov. 28, '35	1	0.984	$\frac{1}{4}F_{\mathrm{KF}}(200)=18.50$
"	"	"	Nov. 29, '35	1	0.917	" 17.86
"	"	"	Nov. 30, '35	1	0.939	" 18.08
"	"	"	Dec. 1, '35	1	0.918	" 17.88
"	"	"	Dec. 3, '35	2	0.914	" 17.84
						Average 18.03

* Fresh sample of NaCl.

leave the briquet at the same angle, the so-called "reflection method" being used. The ionization chamber is moved according to method (1) or (2) above, and the Pliotron circuit readings noted. This constitutes run A. Run B is then immediately made on KF by bringing KF into the beam by means of the motor-driven slide. Going back to LiF, run C is made, and then a second run, D, on KF completes the set. The four runs could be made in about 90 minutes. In computing the power ratios KF/LiF, $B/\frac{1}{2}(A+C)$ and $\frac{1}{2}(B+D)/C$ are used. This is a rough method for correcting for a steady variation of power with time, such as might come from slow deposition of tungsten on the target, or on the cellophane window of the x-ray tube.

As an example of the accuracy attained in relative power measurement, Table II shows some determinations made with Fe $K\alpha$ and Ag $L\alpha$ wave-lengths. We estimate that our structure factors on the short wave-length side of the potassium K absorption edge are accurate to about 2 percent; on the long wave-length side to about 3 percent.

Difficulties and sources of error

In the longer wave-length region, from 3 to 4A, the deposition of tungsten on the target gave some difficulty. Two effects may result from this deposition, (1) a decrease in intensity of the soft line radiation with time, (2) an appearance of higher order diffractions of the tungsten L-series lines superposed on truly soft x-ray diffraction haloes. It was found desirable to use a tube with a shielded filament,[4] which was very satisfactory in removing this source of error.

A curious behavior of NaF in the spectrometer was discovered in some experiments undertaken to detect an effect of particle size, if such existed. Two samples of NaF, which under a microscope showed different average sizes of particles, were placed in the spectrometer and compared. One of the specimens had been used for several weeks; the other was fresh. Contrary to expectation, the fresh specimen, of relatively small particle size, showed a smaller diffracted power in the (200) ring for the Ag $L\alpha$ wave-length. After several days standing in the spectrometer, which was essentially a vacuum desiccator, the two specimens showed equal power in the (200) diffraction haloes. This "aging effect" caused us to question all previous comparisons in which fresh specimens of NaF had been used. We repeated many of these earlier measurements with LiF as the comparison powder. No such anomalous effects were found for LiF.

Orientation of the powders was tested for by brushing the briquet with a camel's hair brush between determinations. No good evidence for such an effect was found.

Where the x-rays fell on the powder a discoloration was produced after some time. To test whether this effect was connected with a change in diffracted power, the samples were shifted slightly so that a fresh spot was selected. No change in diffracted power could be detected.

Schäfer[6] has described an effect of particle size which is equivalent to the statement that with

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[6] K. Schäfer, Zeits. f. Physik **86**, 738 (1933).

very high absorption in the particles the effective absorption coefficient of the material in the briquet is no longer directly proportional to its average density, which relation is tacitly assumed in the expression for the computation of the atomic structure factors, Eq. (2). Our experiments with various particle sizes in NaF at 4.146A could not establish the presence of such an effect.

Experimental results

It may be shown that[7]

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

In this expression the subscripts refer to two different diffraction haloes, either from the same powder or from different powders.

F is the crystal structure factor, Eq. (1).
M is the number of unit cells per unit volume.
j is a factor showing how many orientations of the unit cell can contribute 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.
P_d is the power in the arc of the diffraction halo entering the ionization chamber window.

All of the crystals used were of the NaCl structure, and it can be shown[8] that F can only be 0, or $4(f_a+f_b)$, or $4(f_a-f_b)$ where f_a and f_b are the atomic structure factors of the atoms composing the crystal. In cubic crystals the inverse ratios of the cubes of the length of the sides of the unit cells (a_0) can be used for M_2/M_1. The trigonometric factors of Eq. (2) may be grouped together to give

$$\Phi(\theta)=(1+\cos^2 2\theta)/\sin^2\theta\cos\theta \tag{3}$$

for each reflection. Pertinent data on the crystal powders used are given in Table III. The densities are those computed from x-ray data.

Table III. *Properties of the crystals used.*

Crystal	a_0	Density	M
NaCl	5.628A	2.164	5.610×10^{21}
KF	5.328	2.481	6.612
NaF	4.62	2.809	10.14
LiF	4.01	2.65	15.51

Table IV gives the results obtained for atomic structure factors of KF at various wave-lengths and various values of $(\sin\theta)/\lambda$. All the structure factors in this table are based fundamentally on the value[9]

$\frac{1}{4}F_{\mathrm{NaCl}}(200)=f_{\mathrm{Na}}+f_{\mathrm{Cl}}=20.80$
(1.538A, room temperature).

Based on this value are the two subsidiary standards,

$\frac{1}{4}F_{\mathrm{NaF}}(200)=f_{\mathrm{Na}}+f_{\mathrm{F}}=14.55$
(1.538A, room temperature)

and

$\frac{1}{4}F_{\mathrm{LiF}}(111)=f_{\mathrm{F}}-f_{\mathrm{Li}}=5.00$
(1.538A, room temperature).

Although our experiments on the comparison of LiF and NaCl were actually carried out for Fe $K\alpha$ radiation, we have assumed that the value found is valid for Cu $K\alpha$ radiation. A correction for the variation of the f's of Na and F with wave-length will be discussed later.

Havighurst,[10] assuming a value of 15.75 for $\frac{1}{4}F_{\mathrm{NaCl}}(220)$ at room temperature, obtained $\frac{1}{4}F_{\mathrm{NaCl}}(200)=20.80$, $\frac{1}{4}F_{\mathrm{NaF}}(200)=14.25$, $\frac{1}{4}F_{\mathrm{LiF}}(111)=4.61$. His LiF value does not agree well with that determined by us, and we therefore made several determinations of the LiF : NaCl ratio, as shown in Table II, using different NaCl samples. There is no doubt that our results are

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[7] Compton and Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, 1935). The expression is a combination of Eqs. (6.78), p. 414 and (6.85), p. 419, remembering that (effective absorption coeff.) = (coeff. for particles) [(density of powder)/(density of particles)].

[8] Compton and Allison, reference 7, pp. 354–355.

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

[10] R. J. Havighurst, reference 9, Table I, lists a value of the effective linear absorption coefficient in LiF for Mo $K\alpha$ which is altogether too high according to recent tables of absorption coefficients, for instance, that due to S. J. M. Allen and quoted in Compton and Allison's *X-Rays in Theory and Experiment*. These tables give μ for solid LiF = 3.82 at 0.710A; Havighurst used $\mu=4.59$. The correction to his results seems, however, to increase rather than to decrease the discrepancy between our structure factor and his. In our experiments the iron K radiation passed through a MnO_2 filter which removed almost all the Fe $K\beta$ line.

TABLE IV. *Observed, uncorrected, crystal structure factors.*
Based on $\frac{1}{4}F_{\text{NaCl}}(200)=20.80$.

POWDERS	λ(A)	LINE	ORDERS	θ's	Φ(θ)	j's	μ's	$[P_d]_1/[P_d]_2$	RESULT
NaF : NaCl	1.538	Cu $K\alpha$	(200) : (200)	19° 25′ : 15° 53′	15.42 : 23.92	6 : 6	71.0 : 162.6	2.36	$\frac{1}{4}F_{\text{NaF}}(200)=14.55$
LiF : NaCl	1.934	Fe $K\alpha$	(111) : (200)	24° 41′ : 20° 06′	9.00 : 14.28	8 : 6	69.4 : 312	1.67	$\frac{1}{4}F_{\text{LiF}}(111)=5.00$
KF : NaCl	1.538	Cu $K\alpha$	(200) : (200)	16° 48′ : 15° 53′	21.22 : 23.92	6 : 6	243 : 162.6	0.688	$\frac{1}{4}F_{\text{KF}}(200)=19.00$
KF : NaF	1.538	Cu $K\alpha$	(200) : (200)	16° 48′ : 19° 25′	21.22 : 15.42	6 : 6	243 : 71.0	0.296	$\frac{1}{4}F_{\text{KF}}(200)=19.14$
"	1.934	Fe $K\alpha$	"	21° 18′ : 24° 44′	12.54 : 8.95	"	483 : 139	0.299	19.21
"	2.499	Va $K\alpha$	"	27° 57′ : 32° 44′	6.77 : 4.77	"	960 : 287	0.295	18.56
"	2.744	Ti $K\alpha$	"	31° 00′ : 36° 26′	5.37 : 3.83	"	1174 : 376	0.298	18.20
"	3.353	Ca $K\alpha$	"	39° 00′ : 46° 32′	3.39 : 2.77	"	1997 : 657	0.181	14.94
"	3.432	Sb $L\alpha$	"	40° 06′ : 47° 58′	3.24 : 2.74	"	358 : 705	0.547	10.80
"	3.593	Sn $L\alpha$	"	42° 24′ : 51° 03′	3.02 : 2.75	"	406 : 795	1.18	16.55
"	4.146	Ag $L\alpha$	"	51° 06′ : 63° 49′	2.75 : 3.86	"	602 : 1213	0.936	18.05
KF : LiF	3.593	Sn $L\alpha$	(200) : (111)	42° 24′ : 50° 54′	3.02 : 2.74	6 : 8	406 : 416	1.805	$\frac{1}{4}F_{\text{KF}}(200)=17.22$
"	3.927	Ag $L\beta$	"	47° 29′ : 58° 00′	2.74 : 3.13	"	520 : 542	1.44	17.07
"	4.146	Ag $L\alpha$	"	51° 06′ : 63° 34′	2.75 : 3.82	"	602 : 638	1.25	17.46
							$(\sin\theta)/\lambda$		
KF	1.538	Cu $K\alpha$	(220) : (200)	24° 09′ : 16° 48′	9.44 : 21.22	12 : 6	.265 : .188	0.528	$\frac{1}{4}F_{\text{KF}}(220)=14.75$
"	"	"	(222) : (200)	30° 00′ : 16° 48′	5.77 : 21.22	8 : 6	.325 : .188	0.136	(222) =11.70
"	2.744	Ti $K\alpha$	(220) : (200)	46° 45′ : 31° 00′	2.75 : 5.37	12 : 6	.265 : .188	0.597	(220) =13.86
"	"	"	(222) : (200)	63° 08′ : 31° 00′	3.75 : 5.37	8 : 6	.325 : .188	0.260	(222) = 9.6
"	3.353	Ca $K\alpha$	(220) : (200)	62° 49′ : 39° 00′	3.70 : 3.39	12 : 6	.265 : .188	1.25	(220) =11.33

TABLE V. *Correction for variation of the structure factors of the standard crystals NaF and LiF with wave-length.*

LINE	λ(A)	Δf_{Na}	Δf_{F}	$\frac{1}{4}F_{\text{NaF}}(200)$	$\frac{1}{4}F_{\text{LiF}}(111)$	$\frac{1}{4}F_{\text{KF}}(200)$		$\frac{1}{4}F_{\text{KF}}(220)$	$\frac{1}{4}F_{\text{KF}}(222)$
Cu $K\alpha$	1.538	−0.13	−0.06	14.55	5.00	19.14		14.75	11.70
Fe $K\alpha$	1.934	−0.18	−0.09	14.63	5.03	19.33			
Va $K\alpha$	2.499	−0.25	−0.13	14.74	5.07	18.79			
Ti $K\alpha$	2.744	−0.27	−0.15	14.78	5.09	18.49		14.09	9.7
Ca $K\alpha$	3.353	−0.32	−0.19	14.87	5.13	15.18		11.52	
Sb $L\alpha$	3.432	−0.33	−0.19	14.88	5.13	11.04			
Sn $L\alpha$	3.593	−0.34	−0.21	14.91	5.15	16.96	17.73*		
Ag $L\beta$	3.927	−0.35	−0.23	14.94	5.17		17.64*		
Ag $L\alpha$	4.146	−0.36	−0.25	14.97	5.19	18.57	18.11*		

* LiF used as standard crystal.

uniformly higher than his. James and Firth[11] found a value of $\frac{1}{4}F_{\text{NaCl}}(200)=20.65$ which differs from 20.80 by approximately the correction for anomalous dispersion of the K electrons in chlorine at the Cu $K\alpha$ wave-length.

In spite of the fact that the K-absorption limits of the sodium and fluorine in our standard crystals are far from the wave-length region of the observations, the variation in their f's with wave-length is appreciable and must be corrected for. We have used Hönl's theory in calculating this correction, as given in Eq. (10). The value of Δ for sodium and fluorine has been taken as 0.30. The critical absorption wave-lengths of Na and F were taken as 11 and 18A respectively. Eq. (10) leads to a set of Δf values for Na and F. We have computed the corrected values of $\frac{1}{4}F_{\text{NaF}}(200)$ and $\frac{1}{4}F_{\text{LiF}}(111)$ as follows:

$$\left[\tfrac{1}{4}F_{\text{NaF}}(200)\right]_\lambda=14.55-\left[(\Delta f_{\text{Na}})_\lambda-(\Delta f_{\text{Na}})_{1.54}\right]-\left[(\Delta f_{\text{F}})_\lambda-(\Delta f_{\text{F}})_{1.54}\right],$$

$$\left[\tfrac{1}{4}F_{\text{LiF}}(111)\right]_\lambda=5.00-\left[(\Delta f_{\text{F}}-(\Delta f_{\text{F}})_{1.54}\right].$$

Thus the crystal structure factors of our standards slowly increased with wave-length through the region investigated. The KF structure factors in the last column of Table IV were computed on the assumption of no variation of the NaF and LiF factors with wave-length; the corrected values are shown in the latter columns of Table V.

The values of f_K+f_F thus obtained at room temperature were reduced to values for atoms at rest in the lattice by the general relation $f=f_0e^{-M}$

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[11] James and Firth, Proc. Roy. Soc. **A117**, 62 (1917).

where f_0 is the corrected structure factor and f is the factor observed at absolute temperature T. The value of M is determined by Waller's formula[12]

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

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 has been tabulated by Debye.[13] The value of the characteristic temperature for a crystalline substance may be determined approximately from the Lindemann melting point formula.[14] In this manner the characteristic temperature of KF was found to be 297°K. In reducing the f's to f_0's, a temperature correction was computed separately for each of the two ions in KF, by using the proper mass of each ion for m_a. The values of e^{-M} for each ion are shown in columns 2 and 3 of Table VI. Since in the experiments no diffracted beams from planes in which $\frac{1}{4}F_{\mathrm{KF}}=f_K-f_F$ were measured, no values of either f_K or f_F could be obtained directly from experiment. A value of $f_0{}^F$ was therefore taken from the Hartree[15] curve for the corresponding value of $(\sin\theta)/\lambda$. The f_F was then computed from this Hartree value of $f_0{}^F$ by multiplication with the factor e^{-M_F}. The resulting value of f_F was then subtracted from the observed value of f_K+f_F, leaving a value of f_K. This value of f_K was then reduced by multiplication with e^{M_K} to $f_0{}^K$ and the above value of $f_0{}^F$ added to it, giving $\frac{1}{4}F_0{}^{\mathrm{KF}}=f_0{}^K+f_0{}^F$. The fifth column of Table VI therefore represents the final values of $\frac{1}{4}F_0{}^{\mathrm{FK}}$ from our experiments, and thus those used to compare with theory.

It should be noted that although a theoretically calculated value of $f_0{}^F$ is introduced into the temperature correction, the final result, $\frac{1}{4}F_0{}^{KF}$, has but a negligible dependence upon the value of $f_0{}^F$ which is introduced. Such a value need be known only approximately, since e^{-M_K} and e^{-M_F} differ but little for any of the planes considered. Should another value of $f_0{}^K$ differing by one full electron be chosen, the effect on the final value of $\frac{1}{4}F_0{}^{\mathrm{KF}}$ would be 0.1 electron for the (222) diffraction, and about 0.04 electron for the (200).

TABLE VI. *Temperature corrections applied to the values of $\frac{1}{4}F_{\mathrm{KF}}$ of Table V.*

$\frac{1}{4}F_{\mathrm{KF}}$ Table V	e^{-M_K}	e^{-M_F}	$f_0{}^F$ Hartree	$\frac{1}{4}F_0{}^{\mathrm{KF}}$	INDICES	λ(A)
19.14	0.964	0.930	6.90	**20.10**	(200)	1.538
19.33	"	"	"	**20.30**	"	1.934
18.79	"	"	"	**19.74**	"	2.499
18.49	"	"	"	**19.43**	"	2.744
15.18	"	"	"	**15.98**	"	3.353
11.04	"	"	"	**11.69**	"	3.432
16.96	"	"	"	**17.84**	"	3.593
17.73	"	"	"	**18.64***	"	3.593
17.64	"	"	"	**18.54***	"	3.927
18.57	"	"	"	**19.51**	"	4.146
18.11	"	"	"	**19.03***	"	4.146
14.75	0.933	0.867	5.50	**16.21**	(220)	1.538
11.70	0.900	0.807	4.43	**13.45**	(222)	1.538
14.09	0.938	0.867	5.50	**15.49**	(220)	2.744
9.7	0.900	0.807	4.43	**11.2**	(222)	2.744
11.52	0.938	0.867	5.50	**12.74**	(220)	3.353

* LiF used as intermediate standard.

B. THEORETICAL PART

Statement of the theories

The theory of the variation of the atomic structure factor with wave-length has been developed by Coster, Knol and Prins,[16] Glocker and Schäfer,[17] and Hönl.[18] As the frequency of the primary radiation decreases and approaches the critical frequency of the K electrons, the amplitude of the wave scattered by them increases, becoming much larger than that of the J. J. Thomson scattering. At the same time the phase of the scattered wave changes with respect to that of the incident wave. As a result the scattered wave from the K electrons interferes destructively with the waves scattered from the remaining electrons in the atom, and reduces the resultant amplitude observed at any distant point. The atomic structure factor for an atom is the ratio of the wave scattered by the atom at

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

[13] P. Debye, see Compton and Allison, reference 7, p. 437.

[14] Lindemann, Zeits. f. Electrochemie **17**, 817 (1911).

[15] D. R. Hartree, see Compton and Allison, reference 7, p. 781.

[16] Coster, Knol and Prins, Zeits. f. Physik **63**, 345 (1930).

[17] Glocker and Schäfer, Zeits. f. Physik **73**, 289 (1931).

[18] Hönl, Zeits. f. Physik **84**, 1 (1933); Ann. d. Physik [5] **18**, 625 (1933).

O to a distant point P, to the amplitude which would be scattered to P by a single electron at O, the single electron assumed to be scattering in the J. J. Thomson manner. In order to account for the type of absorption observed in the x-ray region, it has been necessary to replace the K electrons by a distribution of virtual oscillators whose natural frequencies extend from $\nu=\infty$ to the frequency of the K limit. If we empirically distribute these oscillators in such a manner that the absorption coefficient increases as λ^3, and retain the rest of the framework of the Lorentz dispersion theory, we find

$$f(0)=\frac{2\pi mc^2}{e^2\lambda^2}\times\left[\left\{z_K\delta_K+(Z-z_K)\frac{e^2\lambda^2}{2\pi mc^2}\right\}^2+z^2{}_K\beta^2{}_K\right]^{\frac{1}{2}}. \quad (4)$$

In this equation, $f(0)$ is the atomic structure factor in the forward direction (scattering angle zero). z_K is the oscillator strength of the K electrons of the atom of atomic number Z. δ_K is the unit decrement of the refractive index per K electron and β_K is the index of absorption per K electron. The equation assumes that only the K electrons are resonating in the atom.

On the short wave-length side of the K limit

$$\delta_K=\frac{e^2\lambda^2}{2\pi mc^2}\{1+x^2\ln(x^{-2}-1)-2\pi\gamma x^3\} \quad (5)$$

and on the long wave-length side

$$\delta_K=\frac{e^2\lambda^2}{2\pi mc^2}\{1+x^2\ln(1-x^{-2})\}. \quad (6)$$

In these equations, $x=\lambda/\lambda_K$, and γ is a damping constant which we have estimated from the width of the K series lines of potassium. By extrapolation of Parratt's[19] values of the $K\alpha$ line widths of V (23), Ti (22), and Ca (20), we estimate that the $K\alpha$ lines of K (19) have a full width at half-maximum of 1.67×10^{-11} cm. The value of γ is this width divided by the wave-length (3.73×10^{-8} cm) or 4.5×10^{-4}.

We have computed values of β_K according to the following formula:

$$\beta_K=\frac{\lambda A}{4\pi Nz_K}\frac{r-1}{r}\mu_m. \quad (7)$$

Here A is the atomic weight of potassium, N is the Avogadro number, (6.023×10^{23}), r is the absorption jump ratio of the potassium K edge, (10.2), and μ_m is the mass absorption coefficient for potassium for wave-length $\lambda<\lambda_K$. $\beta_K=0$ for $\lambda>\lambda_K$.

In the earliest form of x-ray dispersion theory, due to Kallmann and Mark,[20] the factor z_K which enters the preceding equations was set equal to 2, the electron population of the K shell, according to the Pauli principle. More recent development of the dispersion theory has indicated that for the K electrons at least, an oscillator strength less than 2 should be observed. The reason for this has been clearly stated by Kronig and Kramers.[21] In an atom having only one extranuclear electron, for instance, hydrogen, in its normal state, the sum of the oscillator strengths for all possible transitions, including those to states of positive energy in the continuous region, is one.[22] For a two electron atom however, the second electron may remove one of the possibilities of transition for the first one, by occupying one of the levels to which it could possibly jump. This subtracts a certain oscillator strength from the original electron, and also subtracts a corresponding negative oscillator strength from the second electron, because for it a possibility of emission is removed. Thus the decrement in oscillator strength is transferred from the first to the second electron. In the case of the K electrons, practically all the important discrete levels to which they might go in absorption are already full, and their oscillator strength corresponds to that calculated for transitions into the continuous region alone.

An important quantity in these considerations is Δf, which may be defined as the structure factor decrement. Since the normal value of $f(0)$ is Z, the decrement Δf is $Z-f(0)$. By a

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[19] L. G. Parratt, Phys. Rev. **44**, 695 (1933).

[20] Kallmann and Mark, Naturwiss. **14**, 648 (1926); Ann. d. Physik **82**, 385 (1927).

[21] R. de L. Kronig and H. A. Kramers, Zeits. f. Physik **48**, 174 (1928).

[22] W. Kuhn, Zeits. f. Physik **33**, 408 (1925); W. Thomas, Naturwiss. **13**, 627 (1925).

combination of the preceding equations, it may be shown that on the short wave-length side of the limit

$$\Delta f = Z - \left[\{z_K(x^2 \ln (x^{-2}-1) - 2\pi\gamma x^3) + Z\}^2 + \frac{m^2c^4A^2}{4\lambda^2e^4N^2}\frac{(r-1)^2}{r^2}\mu_m{}^2 \right]^{\frac{1}{2}} \quad (8)$$

and on the long wave-length side

$$\Delta f = -z_K x^2 \ln (1-x^{-2}). \quad (9)$$

These equations are often referred to as those coming from the Kramers-Kallmann-Mark treatment of dispersion theory.

Hönl has made a more fundamental theoretical investigation of the problem than those which led to Eqs. (8) and (9). He computed from theoretical grounds the variation of the absorption coefficient with wave-length, instead of arbitrarily inserting a λ^3 variation law, and computed the oscillator strengths z_K from hydrogen wave functions, making approximate corrections for screening. Hönl's equation for Δf is

$$\Delta f = \frac{2^7e^{-4}}{9}\left[\frac{4x^2 \ln |1-x^{-2}|}{(1-\Delta)^2} - \frac{1}{(1-\Delta)^3}\left\{ x^3 \ln \left| \frac{1-x}{1+x} \right| + 2x^2 \right\} \right], \quad (10)$$

where $\Delta = 0.246$ and represents a correction for screening in the potassium atom. The e appearing in Eq. (10) is the basis of natural logarithms. For large values of x, Eq. (10) approaches the value $\Delta f = 1.43$, which is the oscillator strength of the K electrons of potassium. The values of Δf computed from Eq. (10) are very close to those computed from Eqs. (8) and (9) with $z_K = 1.43$.

Hönl has also investigated the possibility that the Δf values may depend on scattering angle, or on $(\sin\theta)/\lambda$. He finds that although such an effect is theoretically indicated, the magnitude is so small as to be undetectable experimentally except possibly for very heavy atoms. This makes it possible to use the structure factor decrements of Eqs. (8) and (9), computed with $Z = 19$, at the actual scattering angles which can be experimentally realized.

Comparison of theory and experiment

We shall first discuss the comparison of theory and experiment for the variation of $\frac{1}{4}F_0(200)$ with wave-length in KF. In making this comparison, we assume that our measured $\frac{1}{4}F_0(200)$ contains the $\Delta[\frac{1}{4}F_0(200)]$ calculated from Hönl's theory for potassium and fluorine at the wave-length of Cu $K\alpha$ (1.538A). We have

$$\Delta[\tfrac{1}{4}F_0(200)] = \Delta f_0{}^K + \Delta f_0{}^F. \quad (11)$$

The left-hand member of the preceding equation represents the decrement in the reduced crystal structure factor; the right-hand members represent the decrements in the reduced atomic structure factors of potassium and fluorine, and are to be computed directly from Eqs. (8), (9), or (10). The computed value of $\Delta[\frac{1}{4}F_0(200)]$ at 1.538A is -0.38, according to Hönl's theory. Our

TABLE VII. *Comparison of observed and theoretical values of* $\Delta(\frac{1}{4}F_0)$ *in the (200) diffraction of KF.*

LINE	λ(A)	$x=\lambda/\lambda_K$	μ_m	$\Delta f_0{}^K$ Eqs. (8), (9) $Z_K=1.43$	$\Delta f_0{}^K$ Hönl, Eq. (10)	$\Delta(\frac{1}{4}F_0)$# Eqs. (8), (9)	$\Delta(\frac{1}{4}F_0)$# Eq. (10)	EXPERIMENT
Cu $K\alpha$	1.538	0.4486	137	−0.38	−0.32	−0.44	−0.38	(−0.38)
Fe $K\alpha$	1.934	0.5643	272	−0.31	−0.20	−0.40	−0.29	−0.58
Va $K\alpha$	2.499	0.7289	540	−0.03	0.09	−0.16	−0.04	−0.02
Ti $K\alpha$	2.744	0.8006	656	0.36	0.58	0.21	0.43	0.29
Ca $K\alpha$	3.353	0.9785	1128	3.87	4.15	3.68	3.96	3.74
KK abs	3.4277	1.0000	1183	11.02	—	10.83	—	—
Sb $L\alpha$	3.432	1.0013	(125)	8.93	7.78	8.74	7.59	8.03
Sn $L\alpha$	3.593	1.0482	(141)	3.80	3.59	3.59	3.38	1.88, 1.08*
Ag $L\beta$	3.927	1.1146	(179)	2.71	2.56	2.48	2.33	1.18*
Ag $L\alpha$	4.146	1.2096	(204)	2.42	2.33	2.17	2.08	0.21, 0.69*
—	∞	∞	—	1.43	1.43	—	—	—

Values of $\Delta f_0{}^F$ used in computing cols. 7 and 8 from col. 4, Table V.
* LiF used as intermediate standard.

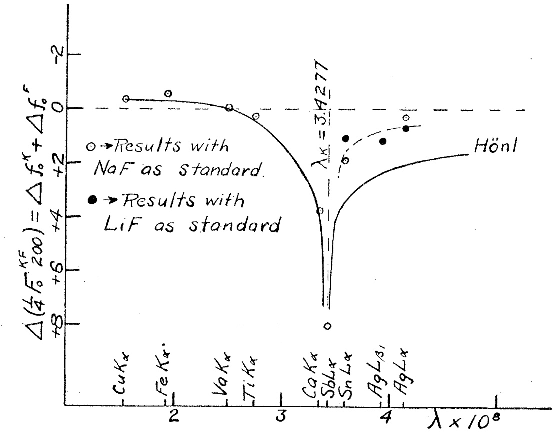

FIG. 2. The wave-length variation of the crystal structure factor for the (200) diffraction of powdered KF. Hönl's theory is the solid curve. The variation of the atomic structure factor of fluorine in this region is so small that practically the entire effect may be ascribed to the potassium K electrons.

measured value of $\frac{1}{4}F_0(200)$ here is 20.10, according to Table VI; hence the value after "correction" for resonance of the K electrons of potassium and fluorine would be 19.72. Thus having fitted theoretical and observed $\Delta[\frac{1}{4}F_0(200)]$ values together at this one wave-length, we can compare theory and experiment at other wave-lengths. This is shown in Table VII.

The experimental values of $\Delta(\frac{1}{4}F_0)$ shown in the last column of the table were obtained in the following way:

$$\Delta[\tfrac{1}{4}F_0(200)] = 19.72 - [\tfrac{1}{4}F_0(200)]_\lambda.$$

The crystal structure factors were taken from column 5 Table VI. The extent of the agreement between theory and experiment is shown in Fig. 2. It is seen that on the short wave-length side of the limit the agreement is within experimental error, but that large discrepancies are found on the long wave-length side. The observed decrements for Sn $L\alpha$, Ag $L\beta$, and Ag $L\alpha$ are considerably less than half those predicted. Taking only the long wave-length side of the curve into consideration, our results agree fairly well with an oscillator strength of the K electrons of about 0.6. Inserting such a result into the equations, however, completely disrupts the observed agreement between theory and experiment at Ca $K\alpha$ on the short wave-length side, and also fails to predict the experimental value for Sb $L\alpha$, which is very close to the limit.

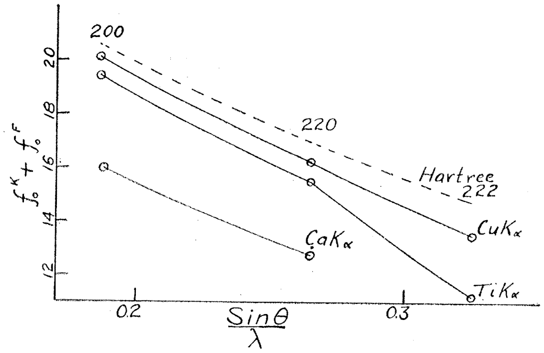

FIG. 3. Variation of the observed structure factor decrements with scattering angle. The point for Ti $K\alpha$ (222) contains a very large experimental error.

It is also interesting to note the extent of the agreement of our results on $\frac{1}{4}F_0(200)$ with the computed structure factors of Pauling and Sherman[23] and of Hartree.[24] From Table VIII it is seen that our measured factors are somewhat lower than the theoretical ones at 1.538A. In computing the theoretical factors in Table VIII, 0.38 has been added to the tabulated values in the references to allow for the resonance of the K electrons of potassium and fluorine at this wave-length. In computing the structure factor for atoms according to Hartree it has been assumed that the K and K^+ curves are indistinguishable at our values of $(\sin\theta)/\lambda$. Our (200) factor is within 0.2 electron of those computed for atoms according to Hartree, but our values fall off more rapidly with $(\sin\theta)/\lambda$ than do his.

Fig. 3 shows an experimental test of the dependence of $\Delta(\frac{1}{4}F_0)$ on $(\sin\theta)/\lambda$. The solid curves represent results taken from column 5 of Table VI. The dashed curve shows Hartree's

TABLE VIII. *Comparison of observed and theoretical atomic structure factor sums at Cu* $K\alpha$, $\lambda = 1.538A$.

INDICES	PAULING AND SHERMAN Ions	PAULING AND SHERMAN Atoms	HARTREE Ions	HARTREE Atoms	EXPERIMENT
(200)	22.0	21.1	20.9	20.3	20.10
(220)	18.0	17.5	17.4	17.2	16.21
(222)	15.5	15.2	15.1	14.9	13.45

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

[24] D. R. Hartree, see Compton and Allison, reference 7, p. 781.

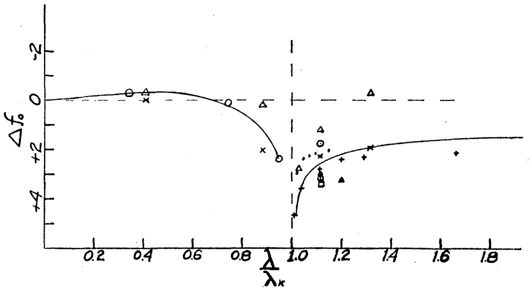

FIG. 4. Results of other observers on the wave-length variation of atomic structure factors in the region of the K absorption edge. The solid curve is Hönl's predicted decrements for iron. The points are experiments on chromium, iron, nickel, and copper.

values for ions at the Cu $K\alpha$ wave-length. If the structure factor decrements are independent of $(\sin\theta)/\lambda$, the solid curves of Fig. 3 should be parallel. This is seen to be very nearly the case with the exception of the curve at the wave-length of Ti $K\alpha$ between (220) and (222). The (222) diffraction halo of Ti $K\alpha$ was the weakest measured in the entire experiment. At the maximum sensitivity of the Pliotron circuit it showed a deflection of about 1 cm above the rather high base-line. Our experimental error for this point is so great that we believe the apparent deviation from parallelism for this point is of no real significance. Our conclusion is that the structure factor decrements are independent of $(\sin\theta)/\lambda$ as predicted for light atoms by Hönl.

C. DISCUSSION OF RESULTS

Résumé of previous work on this problem

Since no previous determination has been made of the variation of the atomic structure factor with wave-length for any atom of as low an atomic number as potassium, no direct comparison of our results with those of other experiments is possible. However, some experimental data are available for atoms of somewhat higher atomic number and the agreement between such data and Hönl's calculations is shown in Fig. 4.

From Eq. (10) it may be seen that Δf is dependent upon the variable λ/λ_K and also on the parameter Δ which is a correction for screening. Since the latter is a very slowly changing function of atomic number, one might consider it almost constant throughout a very limited range of elements of adjacent atomic number. Then Δf would depend to an extremely good approximation upon the variation in λ/λ_K alone. The closeness of this approximation is shown in the table in Hönl's[25] paper. Making use of this fact, the previous experimental data for 24Cr, 26Fe, 28Ni, 29 Cu, have been condensed into a single plot in Fig. 4. The solid curve, which is actually Hönl's curve for iron, represents a very close approximation to the predictions of the theory for all these elements.

As representative of previous work covering a large range of wave-lengths, we have shown the results of Rusterholz[26] on copper (+), of Schäfer[27] on iron (×) and chromium (○), and of Bradley and Hope[28] on the intermetallic compound FeAl (Δ). All of these measurements were made by the photographic method. The values of Rusterholz are from measurements of the (220) diffraction of metallic copper for various wave-lengths, all, however, on the long wave-length side of the Cu K absorption edge. They show good agreement with the calculations of Hönl in the vicinity of the limit, if we assume a value of $f_0^{\mathrm{Cu}}(220)=16$, as indicated by Hartree for the limiting value approached by the atomic structure factor of copper as x approaches zero. At longer wave-lengths than the copper K limit region, Rusterholz's experimental results fall below the Hönl curve. Schäfer's results for iron and chromium are in fairly good agreement also, but the experimental points seem a little higher than theory demands in the immediate neighborhood of the absorption edge on the long wave-length side. This discrepancy is probably within the experimental error. The values of Bradley and Hope are distinctly higher on the long wave-length side and rise to a value equal to the maximum value on the short wave-length side.

Scattered points are also given on the plot showing results for a less complete range of wave-lengths. Both Miss Armstrong[29] and

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[25] Hönl, Ann. d. Physik [5] **18**, 625 (1933), p. 651.

[26] A. A. Rusterholz, Zeits. f. Physik **82**, 538 (1933).

[27] K. Schäfer, Zeits. f. Physik **86**, 738 (1933).

[28] A. J. Bradley and R. A. H. Hope, Proc. Roy. Soc. **A136**, 272 (1932).

[29] Alice H. Armstrong, Phys. Rev. **34**, 931 (1929).

Wyckoff[30] have measured the atomic structure factor for metallic copper (□, ▲) for the wave-length 1.539A using the ionization spectrometer, and Wyckoff has also made measurements with the wave-length 1.655A. Since no temperature correction was applied in either case, proper temperature corrections were made using the values of e^M given by Rusterholz. Since determinations were also made in these two papers of the value of the atomic structure factor of copper using Mo $K\alpha$ (0.710A) radiation; the Δf_0 values plotted above are based upon the experimental value obtained with Mo $K\alpha$. This latter value was made to coincide with the Hönl Δf curve just as in the treatment of our own experiments. A NaCl sample was used as a standard by Miss Armstrong and by Wyckoff throughout the range of wave-lengths which they investigated. No correction has been applied for the small change of the F value of this standard due to resonance of the K electrons of chlorine and sodium. A recent determination of the atomic structure factor of copper for 1.539A radiation has been made by Brindley and Spiers[31] by a photographic method. Their value, which is not plotted, would almost coincide with that of Wyckoff.

Finally there is shown on the plot a series of values of f_0 (●) taken from the dispersion curve obtained by Lameris and Prins[32] using the method of total reflection of the general x-radiation from a mirror of metallic nickel. These readings indicate a steeper rise of the structure factor on the long wave-length side of the absorption edge than the Hönl theory predicts. Direct measurements (not plotted) of the atomic structure factor of nickel by Wyckoff are in good agreement with the points of Lameris and Prins in this region.

Thus it may be said that taken as a whole, the experiments undoubtedly show that the behavior of an atomic structure factor at the K edge is qualitatively that predicted by the modified dispersion theory that has been applied to x-rays. As to quantitative agreement, a general statement is difficult to make. Of the extended surveys, those of Rusterholz and Schäfer seem to confirm the theory in the region of atomic numbers 24 to 29, whereas those of Bradley and Hope and Lameris and Prins lie definitely above the predicted values.

CONCLUSION

Before making a definite statement of our conclusions, we wish to call attention to the manner in which we have treated our experimental data. We have endeavored to keep our values of $\Delta(\frac{1}{4}F_0)$ on as purely an experimental basis as possible. Thus we have not obtained them by subtracting our measured values from a theoretical atomic structure factor sum computed by the method of Hartree or of Pauling and Sherman. Our $\Delta(\frac{1}{4}F_0)$ values of column 9, Table VIII represent differences between an experimental value of $\frac{1}{4}F_0$ at 1.538A and our experimental values at other wave-lengths. A constant has been added in so that Hönl's computed $\Delta(\frac{1}{4}F_0)$ values are fitted to ours at one wave-length (Cu $K\alpha$).

In conclusion we may state the following:

1. *Hönl's calculations do not correctly give the observed structure factor differences for the (200) diffraction from powdered potassium fluoride on the long and short wave-length sides of the potassium K edge.*
2. *The predicted invariance of the structure factor decrement due to K electrons with scattering angle for light elements is confirmed in our experiments.*

The type of discrepancy between theory and experiment is such as to indicate that a revision both of the oscillator strengths and the oscillator distribution functions of the K electrons of the potassium atom in solid KF is necessary.

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[30] R. W. G. Wyckoff, Phys. Rev. **36**, 1116 (1930).

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

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

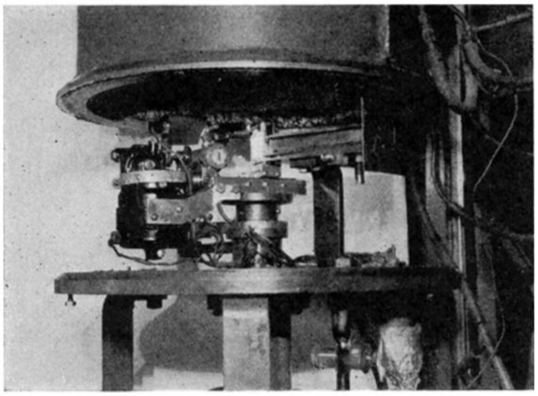

FIG. 1. Photograph of vacuum ionization spectrometer with the cover lifted.