For the sake of completeness the values for the pressures 10, 30, 50 and 100 atmospheres as calculated in the earlier paper are included.

Summary

1. Equilibrium values for the reaction $^1/_2\,N_2 + {}^3/_2\,H_2 = NH_3$ have been determined at 300, 600 and 1000 atmospheres' pressure and at temperatures of 450°, 475° and 500°.

2. Equilibrium constants have been computed for each of the pressure-temperature conditions studied. These constants become larger as the pressure is increased and confirm in this regard the results previously obtained at pressures from 10 to 100 atmospheres.

3. By means of empirical formulas the percentage of ammonia at equilibrium has been calculated for a temperature range of 200–700° and a pressure range of 10–1000 atmospheres.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE JEFFERSON PHYSICAL LABORATORY OF HARVARD UNIVERSITY]

THE EXCITATION, REFLECTION, AND UTILIZATION IN CRYSTAL-STRUCTURE ANALYSES OF CHARACTERISTIC SECONDARY X-RAYS

BY GEORGE L. CLARK[1]

RECEIVED DECEMBER 4, 1923

During the development of a new method of crystal-structure analysis by X-rays, it was discovered that the X-rays characteristic of and excited in the chemical elements in a crystal are reflected by the crystal itself. It was further demonstrated that the reflection takes place both in accordance with the Bragg law, $n\lambda = 2d \sin \Theta$, and also in an anomalous fashion. Some examples of these phenomena, together with a description of the ionization spectrometer utilized in these experiments and of the various steps in the method of analyzing crystals, have already been presented.[2] From the spectra characteristic of the constituent elements it has been possible to determine accurately the spatial distribution of the atoms in potassium iodide, cesium iodide, potassium tri-iodide, cesium tri-iodide, and cesium dibromo-iodide. Thus even cesium and iodine atoms were clearly differentiated, although they are so nearly contiguous in the periodic table and have so nearly the same reflecting power.

It is the purpose of the present paper to present new precision measurements on characteristic spectra, as follows: the iodine K series spectrum from the 100 planes of potassium iodide through five orders; the iodine K series spectrum from the 0001 planes of iodoform, through three orders

---

[1] National Research Fellow.

[2] Clark and Duane, *Proc. Nat. Acad. Sci.*, **8**, 90 (1922); **9**, 117, 126, 131 (1923); *J. Opt. Soc. Am.*, **7**, 455 (1923); *Science*, **58**, 398 (1923).

combined with the tungsten lines characteristic of the target of the Coolidge tube through six orders; the uranium L series spectrum from the 010 planes of uranyl nitrate hexahydrate; and, for purposes of comparison, the fluorescent spectrum of iodine, K series, obtained when powdered potassium iodide is used to scatter the primary X-ray beam from a tungsten target at 90°.

I. The K Series Spectrum of Iodine from Potassium Iodide

A small crystal of pure potassium iodide, 2mm. square and 0.75mm. thick, was set up on the crystal table of the spectrometer. A narrow beam of the general radiation from a tungsten target struck the crystal in such a way as to be reflected from the various sets of planes into the ionization chamber. With the ionization chamber fixed at a convenient angle the crystal was rotated by steps and the ionization current measured by means of a sensitive quadrant electrometer. When these currents are plotted against the crystal table angles, peaks are observed, the angles between which are characteristic of the planes of a cubic lattice. Thus there are planes of major reflecting power at 90° (010), 45° (110), 26.57° (120), 18.43° (130), etc., from the peak representing reflection from one of the cube faces of the crystal (100). It is possible at once to determine experimentally and without assumptions the wave length of the ray, reflected by a given set of parallel planes into the ionization chamber, from the

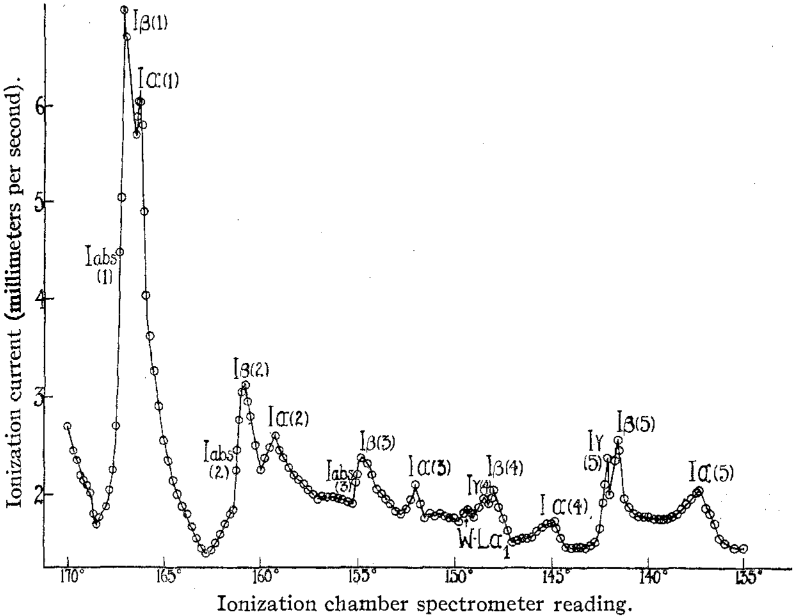

Fig. 1.—Characteristic K series iodine spectrum from $1\bar{0}0$ planes of potassium iodide.

critical voltage, V, at which the ionization current disappears, and the quantum law $Ve = h\nu$, or $\lambda = hc/Ve$, where h, the Planck constant, c the velocity of light, and e the electronic charge, are constants. Substitution of this value of λ in the Bragg law, $n\,\lambda = 2d\ sin\ \Theta$, permits the evaluation of d, the distance between successive parallel planes. From a large number of experiments using wave lengths from the continuous spectrum, the value 3.532×10^{-8} cm. seems very nearly an absolute value for d_{100} of potassium iodide.

A further step may be made by the analysis of the spectrum of the reflection from a set of parallel planes. The process consists in setting the spectrometer on the angular position of a peak, and then rotating both the crystal and the ionization chamber, the latter at twice the rate of the former. The spectrum of the reflection from the 100 planes of potassium iodide appears in Fig. 1. A curve which is the mirror image of this was obtained in this experiment on the opposite side of the zero or direct-beam zone. The angular deviations from the zero of the ionization chamber at 173° 24′ give the values of 2Θ, since the abscissas refer to ionization chamber rather than crystal table angles.

Table I presents the essential data involved in the spectrum curve, in columns as follows: (1) ionization chamber angle; (2) Θ; (3) the wave length, λ; (4) the character of the radiation; (5) the order of the reflection; and (6) the angle, Θ, calculated from $n\,\lambda = 2d\ sin\ \Theta$ upon the basis that $d = 3.532 \times 10^{-8}$ cm.

TABLE I

ANALYSIS OF SPECTRUM REFLECTED BY 100 PLANES OF POTASSIUM IODIDE

$d = 3.532 \times 10^{-8}$ cm.

Ionization chamber angle	Θ	λ	Radiation	Order	Θ calc.
173° 24′	0	....	..	..	......
167° 20′	3° 2′	0.3737	I abs.	1	3° 2′
167° 6′	3° 9′	.3878	Iβ	1	3° 8′ 55″
166° 18′	3° 33′	.437	Iα	1	3° 33′
161° 15′	6° 4′ 30″	.3737	I abs.	2	6° 4′ 30″
160° 47′	6° 18′ 30″	.3878	Iβ	2	6° 18′ 10″
159° 12′	7° 6′	.437	Iα	2	7° 6′ 25″
155° 5′	9° 9′ 30″	.3737	I abs.	3	9° 8′
154° 27′ 30″	9° 28′ 15″	.3878	Iβ	3	9° 29′
152° 0′	10° 42′	.437	Iα	3	10° 41′ 40″
149° 20′	12° 2′	1.473	W-Lα_1	1	12° 2′
149° 0′	12° 12′	0.3737	I abs.	4	12° 13′
148° 30′	12° 27′	.3818	Iγ	4	12° 29′
148° 0′	12° 42′	.3878	Iβ	4	12° 41′
144° 50′	14° 17′	.437	Iα	4	14° 19′ 30″
142° 5′	15° 39′ 30″	.3818	Iγ	5	15° 40′
141° 30′	15° 57′	.3878	Iβ	5	15° 56′
137° 20′	18° 2′	.437	Iα	5	18° 1′

The figure and table lead to the following interpretations. (1) Five groups of peaks appear, marked by sharp absorption drops on the short wave length sides (smaller values of Θ). The wave length corresponding to each discontinuity has been absolutely determined by setting on each point, lowering the voltage applied to the X-ray tube in steps until the ionization current disappears, and calculating from the quantum equation, $\lambda = hc/Ve$. Representative experimental critical voltages for particular points in Fig. 1 are 33,030 for the absorption drop at 167°20′; 32,300 for the peak at 142° 5′; 31,300 for the peak at 141° 30′; 28,250 for the peak at 137° 20′. These correspond, respectively, to the wave lengths 0.3737, (I absorption), 0.3818 ($I\gamma$ detected and measured for the first time), 0.3878 ($I\beta$), and 0.437 Å. ($I\alpha$). The spectrum is therefore characteristic of the iodine atoms in the crystal of potassium iodide.

(2) Substituting the wave length and the angle of the first absorption drop in $n\lambda = 2d \sin \Theta$, gives $0.3737 = 2d \sin 3° 2'$ or $d = 3.532 \times 10^{-8}$ cm., a value identical with that obtained with a wave length from the continuous spectrum. The reflection of these characteristic rays is therefore regular in the sense that the Bragg law is obeyed. It is apparent that any point in Table I will give a value of d within a small fraction of 1% of 3.532×10^{-8} cm., since the agreement between Θ experimentally observed and Θ calculated from this value of d is very satisfactory. The slight discrepancies are not systematic, indicating that the values of λ and of d are as nearly correct as may be ascertained from such experiments.

(3) The spectrum appears only when the X-ray tube is operated above 33,000 volts; that is, the primary beam must contain wave lengths equal to or shorter than the critical absorption wave length of iodine. The spectrum in Fig. 1 was obtained at 65,000 volts. In other experiments with voltages above 69,000, the tungsten line spectrum also appears mixed with the iodine spectrum. Even at 80,000 volts, however, the latter is much more intense than the tungsten spectrum. A comparative energy study of the primary beam at 50,000 and at 78,400 volts shows an enormous difference in the region of the spectrum shorter than the critical absorption wave length of iodine, 0.3737 Å., a fact which is of great importance in the production and detection of both regularly and anomalously reflected iodine rays. Curves illustrating these comparisons will be published soon.

(4) Faint evidence of the strong L_{α_1} line of tungsten at 149° 20′ exists. The enormously greater intensity of the iodine spectrum, however, blots out all but traces of the tungsten L spectrum.

(5) The crystal of potassium iodide may be said to be practically opaque to rays shorter than 0.3737 Å., that is, to those reflected at angles smaller than 3° 2′. In experiments with voltages above 69,000

the first order tungsten K lines at about half this angle are of very feeble intensity. This illustrates the possibility of serious errors in crystal structure analyses where relative intensities of spectral lines are involved, if these lines happen to have wave lengths in the neighborhood of the critical absorptions of the elements in the crystal. Mie,[3] for example, has recently corrected such errors in some of his own interpretations by a study of the characteristic spectra excited and reflected by crystals as discovered by the writer almost two years ago.

(6) The characteristic iodine spectrum lines are more diffuse than the regularly reflected lines characteristic of the X-ray tube target. In none of these experiments by the most careful measurements has it been possible to separate completely γ, β and α peaks in the first order. The β and α peaks are practically separated in the second order, and γ and β are partially separated in the fourth order and completely in the fifth order. The α peak is not resolved into α_1 and α_2 even in the fifth order.

(7) The relative intensities of the various characteristic lines are quite different from those in all target and secondary fluorescent spectra. The β peak is always higher than the α, while for spectra characteristic of targets the intensities stand in the order $\gamma : \beta : \alpha_2 : \alpha_1 = 15 : 35 : 50 : 100$.[4]

(8) I_γ with a wave length 0.3818 Å. is isolated and measured for the first time. It has also been identified, with the same wave length, in the secondary fluorescent spectrum from potassium iodide due to primary radiation from a tungsten target (Section IV).

(9) The relatively great intensity of the fifth order peaks is undoubtedly connected with the fact that within this angular range the anomalous reflection of iodine rays seems to coincide with the regular reflection of iodine rays from the 100 planes. A diagram of the relative positions of the so-called x-peaks as they depend on the angle of incidence has previously been published.[5] Here the extrapolated x-peak lines intersect the line representing reflection from the 100 planes at an ionization chamber angle of about 32°. Table I shows that $I\beta$, fifth order, is reflected into the ionization chamber at 31° 54′. Although one experimenter[6] has not been able to detect this anomalously reflected characteristic radiation, a repetition of the original experiments of the writer both with the ionization spectrometer and with Laue photographs has verified completely those results.[7] Since the discovery of the anomalously reflected iodine rays from potassium iodide, several cases of anomalous

---

[3] Mie, *Z. Physik,* **15**, 56 (1923); **18**, 105 (1923).

[4] Duane and Stenström, *Proc. Nat. Acad. Sci.,* **6**, 477 (1920).

[5] *Ibid.,* **9**, 133 (1923); *J. Opt. Soc. Am.,* **7**, 470 (1923).

[6] Wyckoff, *Science,* **58**, 52 (1923); *Am. J. Sci.,* **6**, 277 (1923).

[7] Clark and Duane, *Science,* **58**, 398 (1923); also an article to be published in *Proc. Nat. Acad. Sci.*

reflection have been reported and explanations attempted, by McKeehan[8] on several metals, Dickinson[9] on potassium iodide and tin tetraiodide, and Mie[3] on bismuth and zinc and lead sulfides.

(10) The excitation of X-rays characteristic of constituent elements and their reflection by the same crystal seems to be adequately explained by the principle of the transfer to matter of radiation momenta in quanta.[10] This analysis alone accounts for all the facts, including the peculiar relative intensities, the diffuse nature of the lines, etc. Mie[3] considers the phenomenon as true optical resonance. If this is true it should be possible by using a voltage between 28,250 and 31,800 to produce an α peak without β and γ peaks. There is every reason to believe in these researches that an α line cannot be produced without the β and γ just as it cannot be produced alone by the target. This point, however, is now being subjected to careful experimental test. Furthermore, if spherical characteristic wave trains, spreading out from atoms in the crystal and reflected from other atoms, produced these effects, then the direction of the reflected beam ought not to depend upon the angle of incidence of the primary X-ray, which it does according to these experiments.

(11) One of the most significant results of the present researches is the repeated accurate proof that a quantum equation $Ve = h\nu$ and an interference equation $n\,\lambda = 2d\,sin\,\Theta$ hold simultaneously and exactly in spite of the apparent incompatibility of a quantum and an interference mechanism. Because of this, however, Duane[10] was led to derive the latter equation entirely upon the basis of a quantum mechanism.

II. The K Series Spectrum of Iodine from Iodoform

In the space lattice of potassium iodide the atoms are presumably ions and the single chemical molecule does not retain its identity, inasmuch as each atom is surrounded by six equidistant atoms of the other kind. Recent work by Bragg indicates that the molecules of organic substances retain their identities in the lattices and that the symmetry of single molecules determines the symmetry of the crystallographic systems. It is of great importance, therefore, to discover whether or not characteristic rays may be excited in and reflected by a crystal of a so-called non-polar organic compound in the same way that the iodine spectrum is obtained from a potassium iodide crystal. For this purpose, and for more definite information concerning the carbon atom, iodoform was selected for analysis.

According to Pope[11] iodoform crystallizes in the hexagonal system with the axial ratio a:c = 1:1.1084. For the X-ray study splendid

---

[8] McKeehan, *J. Optical Soc. Am.*, **6**, 989 (1922).

[9] Dickinson, *Phys. Rev.*, **22**, 199 (1923).

[10] Duane, *Proc. Nat. Acad. Sci.*, **9**, 158 (1923).

[11] Pope, *J. Chem. Soc.*, **75**, 46 (1889).

six-sided crystals were obtained by spontaneous evaporation of a cold acetone solution, and also by allowing a warm, saturated, absolute alcohol solution to cool in a Dewar flask, previously brought to the temperature of the solution. The crystal was oriented on the spectrometer table perpendicular to a $\{01\bar{1}0\}$ face. This enabled reflection from the broad $\{0001\}$ face, and, by rotation through 90°, transmission through the crystal and reflection from parallel planes of the type $\bar{2}110$.

The spectrum of the reflection from the 0001 planes is presented in Fig. 2, and analyzed in Table II. Since the X-ray tube was operated at 78,000 volts, both the iodine lines, through three orders, and tungsten lines, through six orders, appear. The great first order absorption limit of iodine occurs on either side of the direct beam zone at crystal table angle readings of 81° 21′ and 75° 37′, giving Θ a value of 2° 52′. Substituting in the equation $n\lambda = 2d \sin \Theta$, the value of d is found to be 3.737×10^{-8} cm. This is the actual distance between planes containing iodine atoms, regardless of any assumptions as to whether the atoms or the molecules are the lattice units. Again, the agreement between Θ observed for the 25 different points in the spectrum and Θ calculated from $d = 3.737 \times 10^{-8}$

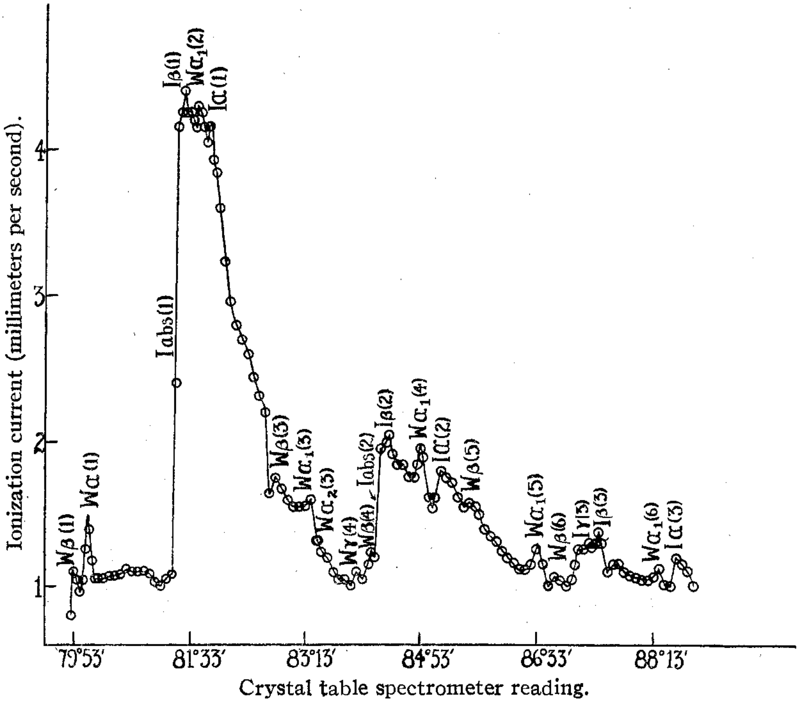

Fig. 2.—Characteristic K series iodine and tungsten spectra from 0001 planes of iodoform.

cm. is remarkable. The complete crystal analysis of iodoform will be the subject of a separate paper.

TABLE II

ANALYSIS OF THE SPECTRUM REFLECTED BY 0001 PLANES OF IODOFORM

$d = 3.737 \times 10^{-8}$ cm.

Crystal table angle	Θ	λ	Radiation	Order	Θ calc.
78° 29′	0	....	..	..	......
79° 53′	1° 24′	0.1842	Wβ	1	1° 25′
80° 5′	1° 36′	.2086	Wα_1	1	1° 36′
81° 18′	2° 49′	.1842	Wβ	2	2° 49′
81° 21′	2° 52′	.3737	I abs.	1	2° 52′
81° 28′	2° 59′	.3878	Iβ	1	2° 58′ 30″
81° 41′ 30″	3° 12′ 30″	.2086	Wα_1	2	3° 13′
81° 50′ 30″	3° 21′ 30″	.437	Iα	1	3° 21′
82° 43′	4° 14′	.1842	Wβ	3	4° 14′
83° 18′	4° 49′	.2086	Wα_1	3	4° 50′
83° 24′ 15″	4° 55′ 15″	.2134	Wα_2	3	4° 54′ 45″
83° 58′	5° 29′	.1790	Wγ	4	5° 30′
84° 8′	5° 39′	.1842	Wβ	4	5° 39′
84° 14′	5° 45′	.3737	I abs.	2	5° 44′
84° 25′	5° 56′	.3787	Iβ	2	5° 57′
84° 55′	6° 26′	.2086	Wα_1	4	6° 27′
85° 10′ 30″	6° 41′ 30″	.437	Iα	2	6° 43′
85° 35′ 30″	7° 6′ 30″	.1842	Wβ	5	7° 5′
86° 33′	8° 4′	.2086	Wα_1	5	8° 4′
86° 43′	8° 14′	.2134	Wα_2	5	8° 12′ 30″
86° 50′ 30″	8° 21′ 30″	.1842	Wβ	6	8° 22′
87° 5′ 30″	8° 36′ 30″	.3737	I abs.	3	8° 37′ 30″
87° 18′	8° 49′	.3818	Iγ	3	8° 49′
87° 27′	8° 58′	.3878	Iβ	3	8° 59′
88° 17′	9° 48′	.2086	Wα_1	6	9° 47′
88° 34′	10° 5′	.437	Iα	3	10° 4′ 30″

III. The L Series Spectrum of Uranium from Uranyl Nitrate Hexahydrate

The K series spectra characteristic of several elements between bromine (35) and cesium (55), excited in and reflected by the same crystal, have been identified in this work. On account of the fact that these spectra differ in several respects from those of the same elements when used as targets in X-ray tubes, as outlined in Section I, an experiment was made with a crystal of uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, in an effort to detect and study the properties of the L series of uranium excited in the crystal and reflected by it. This compound crystallizes in the orthorhombic system in well-formed rectangular plates. The best single crystals were obtained by inoculating a very concentrated solution containing only slightly more water than that furnished by the water of hydration. The X-ray analysis was conducted as in the preceding cases. The spectrum of the reflection from the 010 planes is shown in

Fig. 3 and analyzed in Table III. The peaks on both sides of the spectrometer zero are drawn in this case. The general appearance of the curve is in every way similar to that of the K series spectra. The first tall complex peak comprises four well-defined coalescing peaks. Assigning to the one nearest zero, namely, at 1° 32′, the wave length of the Lγ_1 of uranium, 0.613 Å., the value of d is found to be 11.45×10^{-8} cm. Using this value of d, λ is calculated for the other peaks as tabulated in Col. 3 of Table III, and compared with known values of various lines as tabulated in the fourth and fifth columns.

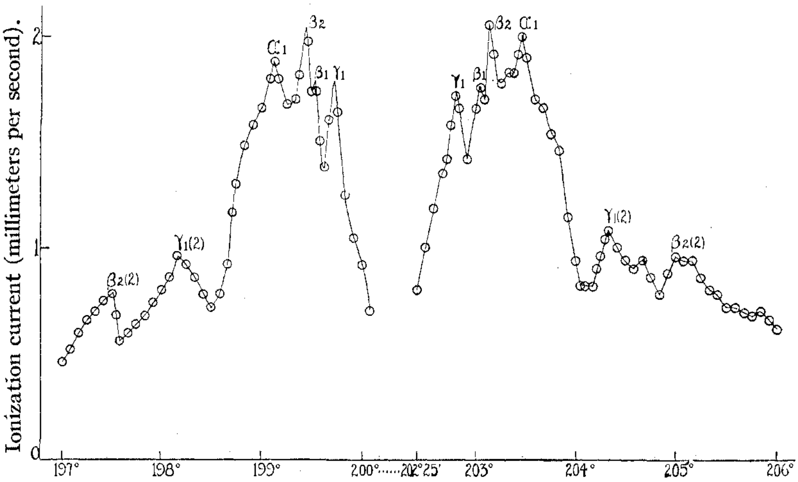

Fig. 3.—Characteristic L series uranium spectrum from 010 planes of uranyl nitrate hexahydrate.

TABLE III

ANALYSIS OF THE SPECTRUM REFLECTED BY 010 PLANES OF URANYL NITRATE HEXAHYDRATE

$d = 11.45 \times 10^{-8}$ cm.

Crystal table angles	θ	γ calc.	Radiation U-L	λ known
202° 47′ 199° 43′	1° 32′	0.6130	γ_1	0.61283
203° 3′ 199° 27′	1° 48′	.7196	β_1	.71807
203° 8′ 199° 22′	1° 53′	.7529	β_2	.75268
203° 27′ 199° 3′	2° 16′	.9095	α_1	.90833
204° 19′ 198° 11′	3° 4′	.6130 (2)	γ_1	.61283
205° 0′ 197° 30′	3° 45′	.7530 (2)	β_2	.75268

It is plainly evident that the four peaks comprising the first large one are respectively due to the γ, β_1, β_2, and α_1 rays in the L series of uranium. Though in ordinary emission spectra β_1 and β_2 have intensities in the ratio 8:6, the latter is much stronger in this type of spectrum because it follows the L_{a_3} absorption limit which has a wave length 0.7214 Å. This

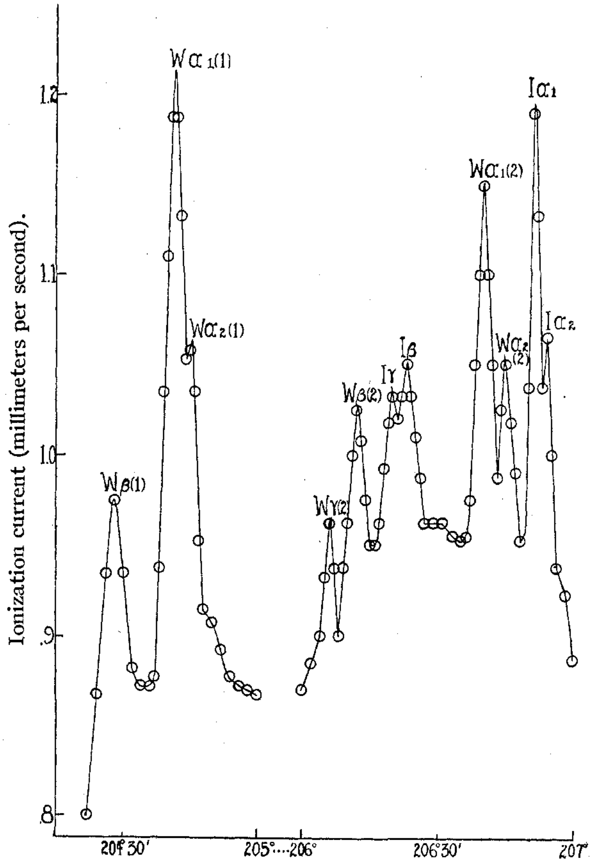

Fig. 4.—Scattered tungsten and fluorescent iodine spectra from potassium iodide as secondary radiator.

is very apparent in the second order. The line α_1 is strongest in ordinary spectra, but here it is weaker than γ and β lines, exactly as in the K series.

The values for d obtained in this way for the three directions at right angles are $d_{001} = 7.93$; $d_{010} = 11.45$; $d_{001} = 13.01 \times 10^{-8}$ cm. The unit parallelopiped contains four molecules, as calculated from the density, 2.807. The uranium atoms are, therefore, at the corners and at the center of the faces, so that the structure is entirely analogous to the unit cubes of nickel nitrate hexammoniate[12] and zinc bromate hexahydrate. Additional details of this analysis will appear in a later paper after further more refined measurements have been made.

IV. The Fluorescent Iodine Spectrum from Potassium Iodide

For purposes of comparison with the characteristic iodine spectrum excited in and reflected by the same crystal, the results of experiments in which primary X-rays from a tungsten target are scattered from powdered potassium iodide are here included. The beam from the face of the target impinges upon a thin pressed layer of finely powdered potassium iodide. The beam of scattered, secondary and tertiary rays at 90° (grazing the surface of the radiator to the primary beam) is analyzed by means of a calcite crystal. The delicacy of this experiment requires the utmost precaution and protection of slits and spectrometer from all rays except those from the secondary radiator under investigation. A diagram of the arrangement of the apparatus with which an extensive series of scattering experiments has been conducted is shown elsewhere.[13]

In Fig. 4 the peaks on one side of zero only are shown. In every case the angle Θ was calculated from the accurately determined angular readings of the same point as it occurred on either side of the direct beam zone. In Table IV, the wave length of a particular point calculated from the angle and from $d = 3.028 \times 10^{-8}$ cm. for calcite is compared with the known wave length of a given radiation.

TABLE IV

ANALYSIS OF BEAM FROM POTASSIUM IODIDE AS SECONDARY RADIATOR AT 90° TO A PRIMARY BEAM FROM TUNGSTEN TARGET

Crystal table angle	Θ	γ calc.	Radiation	λ known
202° 43′	0	...	..	...
204° 28′	1° 45′	0.1849	Wβ	0.1842
204° 41′ 30″	1° 58′ 30″	.2087	Wα_1	.2086
204° 44′ 30″	2° 1′ 30″	.2139	Wα_2	.2134
206° 6′ 15″	3° 23′ 15″	.1789 (2)	Wγ	.1790
206° 12′ 15″	3° 29′ 15″	.1842 (2)	Wβ	.1842
206° 20′	3° 37′	.3818	Iγ	...
206° 23′ 20″	3° 40′ 20″	.3878	Iβ	.388
206° 40′	3° 57′	.2086 (2)	Wα_1	.2086
206° 45′	4° 2′	.2130	Wα_2	.2134
206° 51′ 15″	4° 8′ 15″	.4368	Iα_1	.437
206° 54′	4° 11′	.4417	Iα_2	...

The spectrum contains both the tungsten lines scattered by the radiator and the fluorescent iodine lines. These latter have the same relative intensities and the same wave lengths as those emitted directly by an

---

[12] Wyckoff, THIS JOURNAL, 46, 1260 (1922); *Am. J. Sci.*, 4, 188 (1922).

[13] *Proc. Nat. Acad. Sci.*, 9, 414 (1923).

iodine target. The wave lengths are also the same as those found in Section I for the characteristic spectrum reflected by a potassium iodide crystal. The tungsten lines also have the same wave lengths as those directly from the target. This is not in accord with the ingenious quantum theory of Compton[14] which demands that there should be an increase in wave length for the scattered rays of 0.024 Å., or a shift of the tungsten lines towards larger angles of about 14 minutes. In scattering experiments with a tungsten target tube and graphite, aluminum, sulfur, copper, germanium, molybdenum, silver, potassium iodide, barium chloride, lanthanum oxide, praseodymium and neodymium carbonates (15 elements in all) as secondary radiators, this shift has not been observed—at least the radiation at the calculated angle is not at all comparable in intensity with that of the unmodified ray. On the other hand, it has been possible to detect and measure, particularly with highly polished thin sheets of copper, silver and molybdenum, tertiary X-radiation due to photo-electrons from both the K and the L rings. These radiations appear as broad humps at angles greater than the unchanged tungsten rays taking into account the loss in energy in removing an electron from its orbit. Hence, they should have frequencies which are the differences between the critical absorption frequency of the atoms in the radiator and those of characteristic rays in the primary beam. The remarkable agreement between observed and calculated angles has definitely verified this conclusion. These tertiary rays account for many of the phenomena observed by Compton and by Ross, and yet the mechanism of production is far different from that postulated by the former.[15]

Deepest appreciation is due Professor William Duane of Harvard University, who has been closely associated in all this work, and whose mastery of the science of X-rays has been an inspiration and a powerful guidance.

Summary

1. It is experimentally demonstrated for the first time that X-rays, characteristic of elements in a crystal, are excited in the crystal by a primary beam from a tube, and reflected by it both in accordance with the Bragg law and in an anomalous fashion.

2. Details of a new ionization spectrometer method of crystal analysis are briefly reviewed.

3. A curve showing the characteristic K series iodine spectrum through five orders reflected by the 100 planes of potassium iodide is presented. As an example of a new type of spectrum it is considered in detail. Although the wave lengths are identical with those of characteristic lines

---

[14] Compton, *Phys. Rev.*, **21**, 483 (1923); **22**, 409 (1923); *Phil. Mag.*, **46**, 897 (1923).

[15] Several papers upon experiments with radiators other than potassium iodide are published in the *Proc. Nat. Acad. Sci.*, **9**, 413, 419 (1923); **10** (Jan. 1924).

in spectra of target elements, the spectrum of the secondary rays differs very materially in relative intensities of lines, etc., from that of primary rays characteristic of the same element. The secondary iodine spectrum from a potassium iodide crystal enables a very accurate determination of the distance between planes containing iodine atoms, namely, 3.532 × 10^{-8} cm.

4. An experimental curve showing the iodine spectrum through three orders and the tungsten spectrum characteristic of the tube target through six orders reflected by the 0001 planes of iodoform proves that a non-polar compound is not to be differentiated from a salt such as potassium iodide in this respect. The 0001 interplanar distance in this hexagonal crystal is 3.737 × 10^{-8} cm.

5. A crystal of uranyl nitrate hexahydrate is found to reflect secondary L series uranium rays, enabling the analysis of the spatial distribution of the uranium atoms in the lattice. The unit parallelopiped contains four molecules, is face-centered, and has the parameters in three directions at right angles of 13.01, 11.45, and 7.93 × 10^{-8} cm.

6. The excitation in and reflection by a crystal of X-rays characteristic of elements in it is not an ordinary resonance phenomenon, but is explained, together with all the peculiarities of the spectra, by the principle of the transfer to matter of radiation momenta in quanta.

7. For purposes of comparison a scattering experiment with potassium iodide as secondary radiator is described. The secondary beam analyzed by a calcite crystal proves to contain scattered rays with the same wave lengths as the primary tungsten rays, and fluorescent iodine rays. Evidence of a change in wave length due to scattering by single electrons upon Compton's quantum theory is not obtained in this instance, nor in experiments with 15 other elements.

8. Announcement is made of the discovery and analysis of *tertiary* X-rays produced by the impact upon atoms of secondary electrons which are in turn removed by impact from the K and L rings of atoms in the radiator by the primary beam of X-rays. A tertiary ray has a frequency which is the difference between that of a primary ray and of the critical absorption frequency characteristic of the element of the secondary radiator.

CAMBRIDGE 38, MASSACHUSETTS