

found to be 3.16 volts. Eight breaks in the current-potential curves are recorded, five of which are identified with the Lyman series, the remaining three being ascribed to the hydrogen molecule.

This work was begun while the first author was a National Research Fellow in Chemistry. He takes this opportunity of expressing his thanks to the National Research Council.

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THE REFLECTION BY A CRYSTAL OF X-RAYS CHARACTERISTIC OF CHEMICAL ELEMENTS IN IT

BY GEORGE L. CLARK¹ AND WILLIAM DUANE

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY

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Since our announcement in a former note² of a new method of crystal analysis by X-rays we have made further experiments which have enabled us to detect and study separately the reflections of rays belonging to the characteristic line spectra of the different chemical elements in the reflecting crystal. In the crystals thus far investigated—KI, KI₃, CsI, CsI₃ and CsIBr₂—X-rays characteristic of cesium, iodine and bromine have been identified. These rays, produced by the excitation of atoms in crystals, obey the law $n\lambda = 2d \sin \theta$. They are in addition to and entirely different from the anomalously reflected characteristic X-rays of iodine from KI, reported in another note. Inasmuch as the general phenomenon has not been discovered heretofore, it is the purpose of this note to present a brief summary of the experimental results bearing upon this kind of characteristic reflection.

In the first procedure in the analysis of crystals (l. c.) the ionization chamber is fixed at a convenient angle and the *general* radiation from a tungsten-target Coolidge tube allowed to impinge upon the crystal. By turning the crystal a series of peaks is produced, each one corresponding to reflection from a set of parallel planes in the crystal, such as those designated 100, 110, 120, 130, etc. For a cubic crystal, for instance KI, the 100 and 110 peaks are 45° apart, etc.

In the next step the wave-length corresponding to each peak is determined from the critical voltage and the quantum equation

$$Ve = hc/\lambda, \tag{1}$$

and the perpendicular distance between the given set of planes from the equation

$$n\lambda = 2d \sin \theta. \quad (2)$$

In the case of crystals in which a given set of parallel planes are all alike and equally spaced, the method of analysis just outlined usually suffices. For complex crystals, however, in which the planes may not be alike or equally spaced, the following extension often furnishes important data. This consists in determining the spectrum of the reflection from a set of planes by setting on the peak corresponding to that set, for example the 100 planes, and then changing by steps the angles of both the crystal and the ionization chamber, moving the latter at twice the rate of the former. Instead of finding a series of peaks corresponding to *different* sets of planes, the reflection from the 100 planes *alone* is analyzed.

The spectrum of the 100 planes of KI shows a series of well defined peaks³ decreasing in intensity with increase in the angle, θ . These peaks appear always when the X-ray tube is operated at a potential above 33,000 volts. They cannot be due to reflection of the K-series line spectrum of the tungsten target, since a potential above 69,300 volts is required for its generation. The first peak, at an angle slightly greater than 3° , is characterized by a sharp absorption drop on the short wave-length (smaller angle) side, a peak at the top of this drop, and a smaller, symmetrical but incompletely separated peak on the long wave-length side. It was possible in our experiments to determine at once by the critical voltage method the wave-lengths corresponding to the center of the absorption drop, the higher and the lower peaks. The experiments gave the wave-lengths .374, .388 and .437 Å., respectively. These are the known values of the critical absorption, the K_β and the K_α wave-lengths of iodine. The smaller peaks at larger angles are the higher order reflections of the same characteristic radiations, facts which we checked both by the angle and by the critical voltage measurements of λ .

In more than 10 different determinations with different crystals of KI and using orders to the sixth, we have found the values of d to lie between 3.532 and 3.535×10^{-8} cm. A representative series of data is given in table 1.

In our former note² d_{100} for KI was determined at an angle of 5.51° . The critical voltage was 18,600 volts, corresponding to $\lambda = .6642$ Å. which is a wave-length in the continuous X-ray spectrum. The value of d calculated from this wave-length and this angle coincides with the value calculated from the characteristic line spectrum as in table 1.

A further interesting confirmation that the spectra are characteristic of iodine is obtained from an experiment which we made with the 110 planes and an operating potential of 90,000 volts. *Both* the regular reflection of the line spectrum of the tungsten in the target and that of the secondary

TABLE 1
ANALYSIS OF THE SPECTRUM OF THE 100 PLANES OF KI. (62,000 VOLTS APPLIED TO X-RAY TUBE)

	IONIZATION CHAMBER ANGLE READING	θ	CRITICAL VOLTAGE	λ (FROM CRITICAL VOLTAGE)	DESIGNATION	d $\times 10^8$ CM.
	174°-35'	0°				
Right	168°-30'	3°-2.5'	33,000	.374 Å.	I _{abs.} (1st)	3.532
	168°-15'	3°-10'	31,840	.388	I _{β} (1st)	
	167°-25'	3°-35'	28,400	.435	I _{α} (1st)	
	162°-25'	6°-5'	33,000	.374	I _{abs.} (2nd)	3.532
	162°-0'	6°-18'	31,500	.391	I _{β} (2nd)	
	160°-20'	7°-7.5'	28,250	.437	I _{α} (2nd)	
	156°-21'	9°-7'	(Calcd. 9°-7.5')		I _{abs.} (3rd)	
	155°-30'	9°-32'	(Calcd. 9°-30')		I _{β} (3rd)	
	153°-5'	10°-45'	(Calcd. 10°-45')		I _{α} (3rd)	
Left	180°-40'	3°-2.5'	33,000	.374	I _{abs.} (1st)	3.532
	180°-55'	3°-10'	31,840	.388	I _{β} (1st)	
	181°-40'	3°-32.5'	28,250	.437	I _{α} (1st)	

rays characteristic of iodine atoms in the crystal appeared. In our former note the value of d_{110} was found to be 2.495×10^{-8} cm. from the critical voltage, 26,310 volts, and the corresponding wave-length, $\lambda = .470$ Å., at the angle 5°-30'. Using this value of d the wave-lengths corresponding to each peak appearing in the spectrum were calculated. The remarkable concordance between these calculated wave-lengths and the known true values characteristic of tungsten and of iodine is illustrated in table 2.

TABLE 2
ANALYSIS OF THE SPECTRUM OF THE 110 PLANES OF KI. (90,000 VOLTS APPLIED TO X-RAY TUBE)

CRYSTAL TABLE ANGLE	θ	DESIGNATION	λ (CALCD. FROM $d = 2.495$)	λ (TRUE)
13°-37'	0°			
15°-45'	2°-8'	W _{β}	.185 Å.	.1842
16°-2'	2°-25'	W _{α}	.210	.211
17°-54'	4°-17'	I _{abs.}	.374	.3737
18°-3'	4°-26'	I _{β}	.387	.388
18°-25'	4°-48'	W _{α} (2nd)	.210	
18°-40'	5°-3'	I _{α}	.439	.437

In addition to the check in the value of d_{110} this spectrum shows (1) that the characteristic iodine reflections are more intense than the tungsten lines; and (2) that, whereas the α -peak is always higher than the β -peak for the regular reflected target line spectrum, the reverse is true for radiation characteristic of elements in the crystal. In all such cases so far investigated the α -peak is always *smaller* than the β .

With KI₃, the structure of which will be reported in detail elsewhere, exactly the same kind of characteristic iodine spectra have been obtained as for KI. The first order I _{β} and I _{α} peaks are at 2°-21' and 2°-39'.

Calculating d from $.388 = 2d \sin (2^\circ-21')$ and $.437 = 2d \sin (2^\circ-39')$, the value 4.70×10^{-8} cm. is obtained. At $\theta = 6^\circ-45'$ the critical voltage for the 100 peak is 11,300 corresponding to $\lambda = 1.09 \text{ \AA.}$ and $d = 4.69 \times 10^{-8}$ cm. The crystal unit of KI_3 is a cube slightly distorted into a monoclinic prism, since the angle between the 100 and the 110 planes is $45^\circ-12'$. Wells and Penfield have observed from goniometric measurements a slight inclination of one axis to the plane of the other two. The unit contains $\frac{1}{2}$ molecule. Consequently the original unit cube of KI with $d = 3.532 \times 10^{-8}$ cm. has expanded to an edge length of 4.70×10^{-8} cm. with an extra atom of iodine at or near the center.

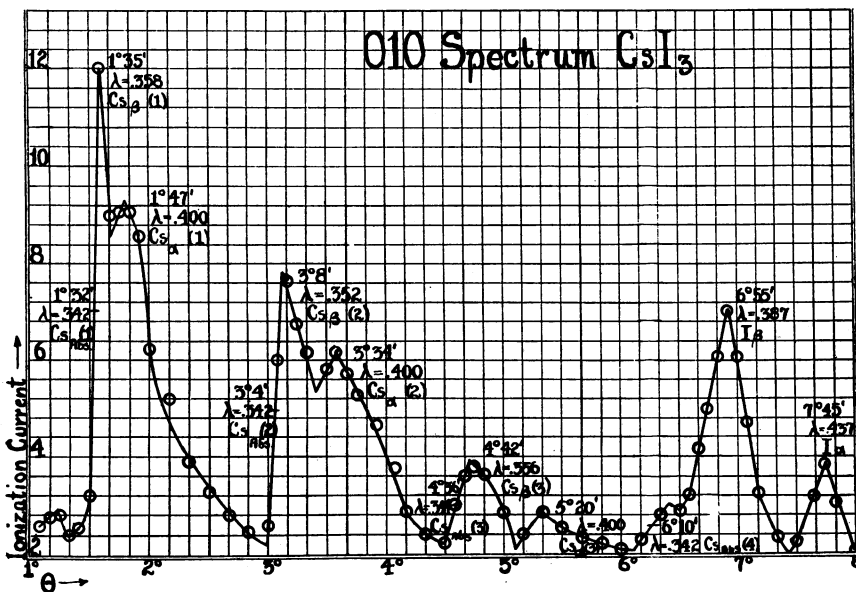


FIGURE 1

One of the most striking cases of characteristic emission from crystal atoms we have obtained with CsI_3 , in which the parallel planes are not alike. Proceeding in the manner described for KI the spectrum for the 010 planes shown in the figure was obtained. Each peak and absorption drop has been labelled with the wave-length obtained by substituting in equation (1) the corresponding *measured* critical voltage. It is found that 4 orders of characteristic cesium peaks appear, and in addition the I_β and I_α peaks at $6^\circ-55'$ and $7^\circ-45'$. Thus it becomes possible to analyze separately the space distributions of both the cesium and the iodine atoms—and this in spite of the fact that cesium and iodine lie so close together in the table of chemical elements.

From the angles and wave-lengths substituted in equation (2) d_{010} for

cesium is 6.43×10^{-8} cm., and for iodine is 1.609×10^{-8} cm. Hence planes containing iodine atoms are $\frac{1}{4}$ as far apart as those containing cesium atoms. We find CsI_3 to be a rhombic crystal (the first of the type to be completely analyzed), for the parameters are different along different perpendicular axes. The spectra of the 100 and 001 planes, however, are like the spectrum of the 010 planes except that the peaks occur at different angles. For the 100 planes the first order Cs_β peak is at $2^\circ-14'$ and the I_β peak at $9^\circ-59'$. Hence d_{Cs} is 4.49 and d_{I} is 1.12×10^{-8} cm. For the 001 planes the first order Cs_β peak is at $1^\circ-26'$ and the I_β peak at $6^\circ-21'$, with corresponding values of d of 7.04 and 1.76×10^{-8} cm. The crystal unit therefore must be a rectangular parallelepiped with cesium atoms at each corner and iodine atoms at the center and equidistant along the body diagonal. From symmetry considerations the diagonals are probably distributed in the same way as those of FeS_2 .⁴

With CsIBr_2 , also a rhombic crystal with the values of d equal to 4.26×10^{-8} cm. (100), 5.91×10^{-8} cm. (010), and 6.90×10^{-8} cm. (001), the first order spectrum peak is more complex since it contains the characteristic effects of both cesium and iodine. These are, however, completely separated in the higher orders with remarkable distinctness. The iodine planes in this case are the same distance apart as the cesium planes. Singularly a tall peak appears for the 100 spectrum at $6^\circ-28'$, between the second and third order cesium and iodine peaks. If this has a wave-length of .929 Å., the K_β of bromine, then d_{Br} comes out such that a bromine plane lies exactly midway between a cesium and an iodine plane. The analysis of this crystal is, however, incomplete and will be reported in detail after further investigation. Crystals of CsIBrCl and RbICl_2 are also being studied in the hope of detecting the reflected X-rays characteristic of chlorine, as well as of the other heavier elements.

The reflection of characteristic X-rays described in this note seems to be reasonably well explained by the assumption (mentioned in our first paper) that a primary X-ray excites secondary characteristic X-rays in atoms with a certain time lag, approximately the same for all atoms of one kind. It is not necessary to assume that the primary ray has wave-lengths, but only that it must have been produced by a voltage above certain critical values. If the secondary rays have wave-lengths they will interfere and produce beams in the required directions. This point of view, however, does not appear to be compatible with the law of the conservation of energy applied to the processes going on in individual atoms.

¹ NATIONAL RESEARCH FELLOW.

² These PROCEEDINGS, 8, 90 (May, 1922).

³ Curves illustrating this spectrum will be published shortly.

⁴ Bragg, *X-Rays and Crystal Structure* (1916), p. 132.