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CHANGE OF FREQUENCY OF X-RAYS SCATTERED BY BOUND ELECTRONS

By Dana P. Mitchell

Abstract

This is a report of the detailed investigation which followed the discovery of "fine structure in scattered x-rays" reported in April, 1928. Molybdenum $K\alpha_1$ x-rays were scattered at about 90° by graphite, aluminum and beryllium. Lines from graphite were shifted 0.0013, 0.0023 and 0.0113A to the long wave-length side of Mo $K\alpha_1$. From aluminum the shifts were 0.0023, 0.0055 and 0.069A to the long wave side of Mo $K\alpha_1$. From beryllium the shifts were 0.0048A to the long wave-length side and 0.00065A to the short wave-length side of Mo $K\alpha_1$. Graphite shifts for scattering angles of 42° and 147° were the same as for 90°. This and all curve widths establish the fact that the scattering electrons were ejected with zero kinetic energy. Hence the energy relation is $h\nu^1 = h\nu \pm Ve$. From this the *critical potentials;* 32, 57 and 279 volts are obtained for carbon; 57, 136 and 1550 volts for aluminum; 16 and 119 volts for beryllium.

Introduction

SINCE the first spectroscopic investigation of the change of frequency of scattered x-rays[1] there has always appeared an "unmodified" line as well as the "modified" or "Compton" line. This unmodified line has been so called because within the experimental error it has in each case appeared in the same position as that of the initial rays being scattered. However, in photographic spectra the resolution was in the best case[2] just enough to resolve the $K\alpha_1$ and $K\alpha_2$ lines of molybdenum, and in the ionization spectra even this resolution seems to have been unobtainable.

The chief obstacle to better resolution has been that when sufficiently narrow slits were used either singly or in multiple[3] the energy was diminished below the limit of practical measurement. Investigation of possible fine structure of this line was therefore impractical until the development of the two-crystal x-ray spectrometer by Davis and Purks.[4] With this instrument the heretofore unobtainable, very high, resolution, independent of the width

[1] A. H. Compton, Phys. Rev. **21,** 715 and **22,** 409 (1923).

[2] Ross's Spectrum of MoK series scattered at 55° by paraffin, shown before the A. A. A. S. and Am. Phys. Soc. in December 1923.

[3] W. Soller, Phys. Rev. **23,** 292 (1924).

[4] Bergen Davis and Harris Purks, Proc. Nat. Acad. **13,** 419 (1927).

of slits used, is obtained. This property which permits the use of wide slits without diminution of resolution is invaluable in the investigation of the spectra of such weak radiations as scattered x-rays.

As an illustration of this increase in resolution of scattered x-rays, the author's ionization, wave-length curves[5] obtained by means of a Soller slit[3] and single crystal are 0.014A wide at half maximum while those obtained with the "two-crystal method" are but 0.0006A wide.

In the former the $K\alpha_1\alpha_2$ x-rays of molybdenum give a single broad "rocking curve" and are not resolved, but in the latter Mo $K\alpha_1\alpha_2$ appear as two narrow rocking curves that are widely separated from each other.

The experimental work of this paper is the detailed investigation which followed the discovery of "fine structure in scattered x-rays" (on March 9, 1928) that was reported to the American Physical Society[6] during its April meeting that year, and later described in detail.[7]

Apparatus Details

In each experiment the scatterer was placed between two molybdenum anodes, (1) the anodes being in separate cylindrical tubes or (2) in a single bulb containing the scatterer. (See Fig. 1)

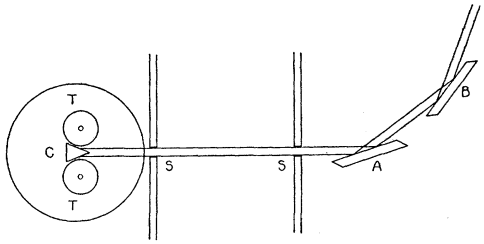

Fig. 1. Diagram of apparatus. *T*, *T*, x-ray tube anodes; *C*, scattering element; *S*, *S*, slits; *A*, collimating crystal; *B*, analyzing crystal.

The scattering investigated was in each case that of Mo $K\alpha_1$ x-rays. Scatterers used were in the order given, graphite, aluminum, and beryllium.

The following may also be of interest:–

Crystals: A previously tested cleaved pair of calcite (Ice-land spar).
Reflection order: First order on each crystal.
Slit width: 2.5 to 3 mm. (Note: this has nothing to do with curve width.)
Slit height: about 2 cm.
Tube power: constant d. c. Maximum potential 42 Kv. Maximum current 85 m.a.
Note: Even with wide slits the very low power of the scattered x-rays is still the chief obstacle to the analysis of these rays.
Electrometer sensitivity: about 2500 mm per volt at one meter.
Ionization system capacity: about 50 cm.
Note: Difficulty here is ratio of ionization produced by x-rays to variable ionization from uncontrolled sources.

[5] Never published. Similar curves were published by A. H. Compton and Y. H. Woo, Proc. Nat. Acad. **10,** 271 (1924).

[6] Mitchell and Davis, Phys. Rev. **31,** 1119 (June, 1928).

[7] Bergen Davis and D. P. Mitchell, Phys. Rev. **32,** 331, (1928).

Experimental Results

Carbon: With a graphite wedge placed so that the right section of the spectrometer slits was equally divided by its edge, the Mo $K\alpha_1$ x-rays scattered at about 90° were analyzed.

A typical spectrum is shown in Fig. 2.

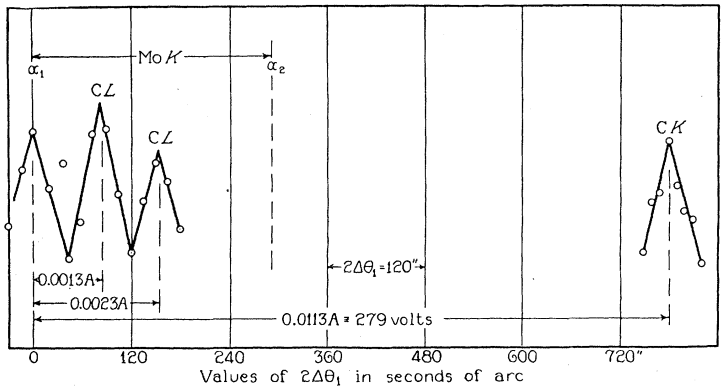

Fig. 2. Typical spectrum of Mo $K\alpha_1$ scattered by bound electrons in graphite.

From such spectra the following data are obtained.

Observed line	$2\Delta\theta_1$	$\Delta\lambda$
Mo $K\alpha_1$	0	0
1st shifted	90″	0.0013A
2nd shifted	158″	0.0023
3rd shifted	780″	0.0113

These values of $2\Delta\theta_1$ are probably not more accurate than $\pm 10''$ which is equivalent to ± 0.00015A.

The half maximum width of each of these rocking curves is about $2\Delta\theta_1 = 40''$ or 0.0006A. In connection with these widths it is well to note that the divergence of the radiation incident on the scatterer was in some cases nearly 90° and yet the curves were of the same width herein noted.

Spectra of radiation scattered by graphite at about 42° and 147° with a divergence of only 5° show similar displacement and curve widths. These latter spectra are less satisfactory because less energy was obtainable.

Aluminum: A typical spectrum of Mo $K\alpha_1$ x-rays scattered by a wedge of aluminum placed as described above, is shown in Fig. 3.

Such spectra yield the following displacements:

Observed line	$2\Delta\theta_1$	$\Delta\lambda$
1st shifted	160″	0.0023A
2nd shifted	380″	0.0055
3rd shifted	($2\theta_1 = 14°44'$)	0.069

The first two values of $2\Delta\theta_1$ are probably not more accurate than $\pm 15''$ or ± 0.0002A and the third about $\pm 2'$ or ± 0.002A. The half maximum width of these lines appears to be a little greater than those from graphite but not more than 50″ or 0.0007A. All spectra of scattering by aluminum

were for about 90° scattering angle and about 45° divergence of the incident radiation

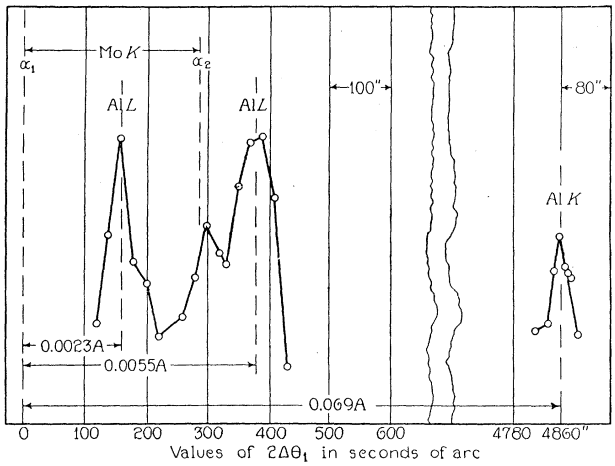

Fig. 3. Typical spectrum of Mo $K\alpha_1$ scattered by bound electrons in aluminum.

Beryllium: The spectrum of Mo $K\alpha_1$ x-rays scattered at about 105° by a block of beryllium is shown in Fig. 4. The average displacements are:

Observed line	$2\Delta\theta_1$	$\Delta\lambda$
1st shifted	$-45''$	-0.00065A
2nd shifted	$334''$	0.0048

The first displacement is probably good to $\pm 10''$ or 0.00015A and the second to $\pm 15''$ or 0.0002A. The half maximum width of the first is not

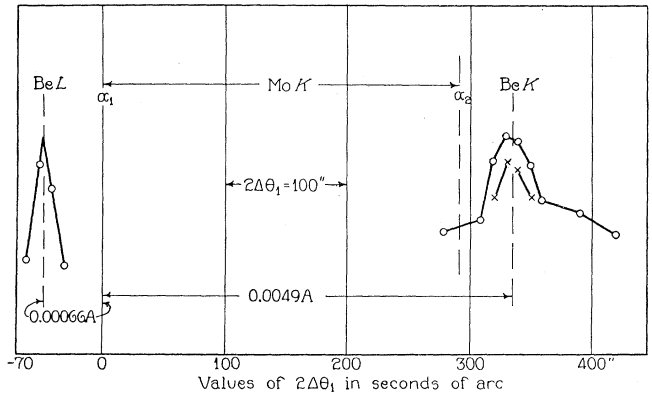

Fig. 4. Typical spectrum of Mo $K\alpha_1$ scattered by bound electrons in beryllium.

over $30''$ and the second about $35''$ or an average of 0.0005A. The most notable thing in the case of beryllium is that $2\Delta\theta_1$ and $\Delta\lambda$ for the first shifted line are negative. This will be discussed later.

Discussion

The effect of binding on the change of wave-length of x-rays scattered by bound electrons has been discussed at length by A. H. Compton[8] and G. E. M. Jauncey.[9] Both reached the conclusion that when the scattering electron is ejected, the shift in wave-length will probably be

$$\Delta\lambda=\lambda^2/(\lambda_s-\lambda)+(h/mc)\ \text{vers}\ \phi \tag{1}$$

where λ_s is the critical absorption wave-length for the stationary state from which the bound electron was ejected, and ϕ is the angle between incident and scattered quanta. The first term in this expression represents the shift due to the loss of enough energy to release the bound electron; and the second term, the shift due to loss of kinetic energy and momentum given to the *now* free electron.

In these experiments ϕ was about 90° so the second term in Eq. (1) would be about 0.024A for *all* scattering elements, yet nearly all of the *observed* shifts are much less than this. It would therefore appear that the scattering electron must have zero kinetic energy after ejection.

In this case the energy relation is simply

$$h\nu'=h\nu-Ve \tag{2}$$

where V is the critical potential and the shift will be

$$\Delta\lambda=\lambda^2/(\lambda_s-\lambda) \tag{3}$$

If we substitute Thibaud's[10] value of λ_s for K energy level of carbon in Eq. (3) we have

$$\Delta\lambda=0.708^2/(43.5-0.708)=0.0117A.$$

This may be compared with the corresponding value for carbon here observed $\Delta\lambda=0.0113$A.

Likewise using Fricke's[11] value $\lambda_s=7.947$ for K energy level of aluminum we have

$$\Delta\lambda=0.708^2/(7.947-0.708)=0.069\text{A}.$$

This is identical with $\Delta\lambda=0.069$A here observed.

The agreement is so good it seems necessary to conclude that the K *electrons are ejected with zero final kinetic energy.*

Such agreement is however not the only basis for this conclusion. If the x-ray quantum incident on the scattering electron imparted kinetic energy to that electron, momentum would also be imparted. The amount of this kinetic energy would depend upon the momentum and hence upon the relative direction of the scattered and the incident x-ray quanta. That is,

[8] A. H. Compton, Phys. Rev. **24,** 168 (1924); also X-rays and Electrons (D. Van Nostrand).

[9] G. E. M. Jauncey, Phys. Rev. **25,** 314 and 723 (1925).

[10] J. Thibaud, Compte Rendus **186,** 308 (1928).

[11] H. Fricke, Phys. Rev. **16,** 202 (1920).

$\Delta\lambda$ would depend upon the angle ϕ of scattering. Observations at different angles of scattering by graphite showed $\Delta\lambda$ to be independent of angle. That $\Delta\lambda$ is independent of scattering angle for graphite, aluminum and beryllium is also shown by the extremely narrow rocking curves obtained in all cases; curves of practically the same width as the initial Mo $K\alpha_1$. Variation of $\Delta\lambda$ with angle is incompatible with such narrow curves for in most cases the divergence of the incident radiation was so great that if $\Delta\lambda$ did vary with scattering angle, the resulting scattered radiation would be a band of many different wave-lengths, the rocking curve for which would be very wide. This important conclusion was pointed out by Davis and Mitchell[7] in the previous paper.

Beryllium; an unusual case. The change in frequency (Ve/h) of x-rays scattered by the outer electrons of beryllium is opposite in sign to that indicated by Eq. (2).

Instead of the scattering electron being ejected from a "bound" position and absorbing energy Ve from the energy $h\nu$ of the quantum being scattered, it appears that the scattering electron was free or nearly free and in scattering it (the electron) moved into a state (L level) of less energy and in so doing *added* its loss of energy to the quantum being scattered, i.e. in this case $h\nu' = h\nu + Ve$.

It is also remarkable that the *loss* of energy (Eq. 2) observed in the case of carbon and aluminum was not observed in the case of beryllium. Further investigations may disclose both kinds of energy transfers. The question of probability of "kind" is however a very interesting one that is as yet unanswered.

Raman and Krishnan[12] and others have observed both kinds of scattering of optical quanta by molecules and here also the explanation is incomplete

Critical Potentials

Since it is established that the only change in the energy of the x-ray quantum being scattered in these experiments is equivalent to the energy necessary to eject the scattering electron, we may write

$$h\nu' = h\nu \pm Ve \tag{4}$$

and compute the critical potentials indicated by this equation. These critical potentials computed from the observed data are shown in Table I.

Table I. *Critical potentials.*

Scatterer and (Z)	Critical potentials in volts Outer levels		K
Be (4)	16 ± 4		119 ± 5
C (6)	32 ± 5	57 ± 5	279 ± 5
Al (13)	57 ± 5	136 ± 5	1550 ± 40

[12] C. V. Raman and K. S. Krishnan, Indian Jl. of Phys. Mar. 31 and July 31, (1928).

K electrons. Table II was prepared to facilitate comparison of these values for K energy levels with those of other observers. The agreement is well within the experimental error.

TABLE II. *Comparison of K critical potentials with those of other observers.*

Reference	Be ($Z=4$) V	ν/R	C ($Z=6$) V	ν/R	Al ($Z=13$) V	ν/R
Table I	119 v.	8.8	279 v.	20.7	1550 v.	114.7
Bul. Nat. Res. C.[13]	121	9.0	288	21.3	1570	115.9
McLennan and Clark[14]	104	7.7				
Kurth[15]			283	20.9		
Thibaud[10]			284	21.		
Fricke[11]					1550	114.7

Outer electrons. The critical potentials here obtained for the outer electrons do not agree so well with earlier determinations. There are however significant differences between values deduced from wave-length measurements in the extreme ultra-violet spectra of gases and those determined by means of the photoelectric action of the emitted radiation from solids.

In Table III are shown a number of these earlier determinations together with those from this investigation. The latter were placed in the first row of this table in order to provide a convenient means of comparison

TABLE III. *Critical potentials of outer electrons.*

Reference	Be (4)	C (6)		Al (13)	
Table I	16 v.	32 v.	57 v.	57 v.	136 v.
Mean values from		11.2			
Bul. Nat. Res. C.[13]	8	34		67	128
Horton Andrews				66	107
and Davies[16]				42	
Hughes[17]		34.5			
Kurth[15]		32.9		37.9	123
McLennan	16				
and Clark[14]	20.3		74		
Millikan	9.5	11.3	45.5		
and Bowen[18]	18.1	24.3	64.2		

That the observed values do not agree with those from the Bulletin of the National Research Council[13] is not surprising since most of those are for the gaseous state. The outer electrons are known to be most effected when gas atoms are brought into close proximity of the solid state. The critical potentials should increase although possibly not so much as here indicated.

The heat of formation is insufficient to account for these differences between gaseous and solid state. The maximum probable value for the heat

[13] Bull. Nat. Res. Council No. 48 (1924).
[14] McLennan and Clark, Proc. Roy. Soc. (A)102 (1923).
[15] E. H. Kurth, Phys. Rev. 17, p. 528 and 18, p. 461 (1921).
[16] F. Horton, U. Andrews and A. C. Davies, Phil. Mag. 46, 721 (1923).
[17] A. L. Hughes, Phil. Mag. 43, 145 (1922).
[18] R. A. Millikan and I. S. Bowen, Phil. Mag. **4**, 561 (1927).

of formation of graphite, 250 kilo-calories per mole, is about 10 equivalent volts. Obviously this is not enough to account for the lack of agreement of the critical potentials here observed and those found for gases.

The agreement of the determinations from solids is in general more satisfactory. The probable precision of this investigation indicates that the outer electrons' critical potentials in Table I are the most accurate yet obtained for these solids.

Multiple Ionization

In this investigation of scattered radiation the scattering substance was radiated with a great abundance of general radiation from about 0.3A upwards. This fact suggests that possibly a majority of the scattering atoms were already partially ionized. In this case the observed critical potentials might be expected to be somewhat greater than those observed for stripped atoms by Millikan and Bowen.[18] Such agreement however is not very good even though the lack of a line in the scattered spectra corresponding to initial ionization in gases be explained by assuming that such ionization was produced by the general radiation, or that the valence electron lost its identity in the solid.

An alternative speculation is that for some unexpected reason two or more electrons are removed by one quantum from one atom, as a single act. In this case the data from enhanced spectra indicate the values here observed are too small.

After the foregoing considerations it seems that attempts to explain these discrepancies on the assumption of multiple ionization are fruitless until additional and more precise data are available.

Conclusion

In conclusion I would recall attention to the observed data set forth (Experimental Results) which fully establish the existence of *the change of frequency of x-rays scattered by bound electrons that are ejected with zero final kinetic energy.*

For his keen interest and assistance in this work and for many privileges in his laboratory, I wish to express my appreciation to Professor Bergen Davis.

Columbia University,
New York, N. Y.
March 4, 1929.

Note added in proof: In view of Ehrenberg's (Zeits. f. Physik **53,** 234, 1929) failure to observe the change in wave-length of Mo x-rays scattered from Acheson graphite and his suggestion that my results were due to uranium impurity it should be pointed out that since obtaining these results on Acheson graphite I have verified them by observing the x-rays scattered from a piece of pure carbon supplied by the General Electric Company.