conduction electrons in metals demands that the component velocity distribution at ordinary temperatures be parabolic, the structure of the Compton band scattered by these electrons is therefore also parabolic.

In conclusion, the point of this note was implicit in the author's papers[3, 4] of 1925 and in DuMond's paper[5] of 1929 but so far as the author knows has not been stated explicitly before.

OCTOBER 15, 1934 PHYSICAL REVIEW VOLUME 46

Effect of Electron Binding upon the Magnitude of the Compton Shift

P. A. Ross and Paul Kirkpatrick, *Department of Physics, Stanford University*

(Received July 24, 1934)

Precision measurements of the Compton shift for ninety degree scattering of the wave-lengths 0.435A, 0.496A and 0.631A by carbon and by beryllium have been performed, using the ring-target x-ray tube and a double spectrometer, under the assumption that the mean shift for two mutually supplementary angles of scattering equals the ninety degree shift. In all cases the observed shift is less than h/mc, the value required by the Compton formula, the maximum percentage discrepancy being 2.4 percent, observed in the case of λ0.631A scattered from carbon. These observations fulfill the predictions inherent in Wentzel's theory of scattering by bound electrons, and are consistent with the explicit shift formula previously deduced by the present authors, as regards dependence of the shift upon wave-length and upon ionization energy of the scatterer. They are also in satisfactory quantitative agreement with the theoretical shift formulas of F. Bloch.

Introductory

THE announcement of the observation of scattered x-rays of modified wave-length by A. H. Compton[1] in 1923 was accompanied and supported by a theory so concise and acceptable, and so nicely confirmed in a number of laboratories, that less attention has been paid in subsequent years to possible minor inaccuracies in the original description than would have been devoted to the aftermath of a discovery less completely set forth in the first instance. The early shift measurements of Sharp[2] and of Kallmann and Mark,[3] agreeing satisfactorily with the Compton equation $\Delta\lambda=(h/mc)(1-\cos\varphi)$, operated to establish this equation as correct within the limits of possible observation. More recent experiments by Nutting[4] have resulted in values of the 90° shift which are from one to two percent lower than the value h/mc required by Compton's equation. Nutting also remarked that the mean of all determinations available in 1930 was somewhat below h/mc but considered this to be a result of experimental error and concluded that the experiments as a whole were in agreement with the Compton formula.

The incompleteness of the type of treatment employed by Compton had been considered, however, by Wentzel,[5] in whose theory of scattering we may discern the implicit requirement that the wave-length modification occasioned by scattering by bound electrons shall be less than that expected of the practically free electrons of Compton. Wentzel's treatment does not provide an explicit shift formula, comparable in simplicity to the Compton equation given above. Such an equation has been deduced by the present authors[6] from relatively simple energy and momentum considerations, and Bloch[7] has derived a similar and more complete relation upon the broader basis of wave mechanical theory. The present paper offers experimental evidence relevant to this question, in the form of results of precision measurements of the wave-length shifts accompanying the scattering of radiations of three different wave-lengths by carbon and by beryllium.

[1] A. H. Compton, Phys. Rev. **21**, 483 (1923).
[2] H. M. Sharp, Phys. Rev. **26**, 691 (1925).
[3] H. Kallmann and H. Mark, Naturwiss. **14**, 3 (1925).
[4] F. L. Nutting, Phys. Rev. **36**, 1267 (1930).
[5] G. Wentzel, Zeits. f. Physik **43**, 1, 779 (1927).
[6] P. A. Ross and Paul Kirkpatrick, Phys. Rev. **45**, 223 (1934).
[7] F. Bloch, following paper.

Apparatus

It is probably safe to state that the difficulties encountered in the spectrometric study of scattered x-rays all result from the weakness of these radiations. We have found it possible to overcome these difficulties to a large extent by using as a source the ring-target x-ray tube previously described.[8] This source combines a target area of about 10 cm² with good constancy of scattering angle. The principle of this tube and the geometry of its use in shift measurements are illustrated in Fig. 1. The focal ring is the complete locus of

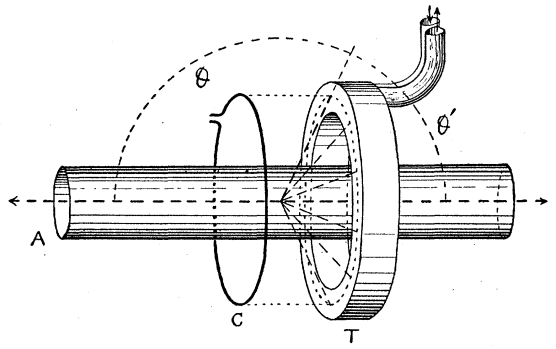

FIG. 1. Schematic representation of the ring-target x-ray tube for the study of scattering. C is a tantalum filament (support not shown), and T the hollow annular target, supported by its cooling tubes. A is a thin-walled and open-ended aluminum tube to enclose the scatterer. External walls of x-ray tube not shown. With the scatterer at the point of convergence of the rays indicated by broken lines from the focal ring, radiation emerges from the aluminum tube after undergoing scattering at the mutually supplementary angles θ and θ'.

x-ray sources consistent with a given angle of scattering from a concentrated scatterer. The scattering angle is controlled by the position of the scattering body in the tube which lies along the target axis. Mutually supplementary angles of scattering are available at all times, since the scatterer sends radiation both ways along the tube axis. This is an important matter since, as shown below, it liberates us from that bugbear of shift measurements: uncertainty of scattering angle. There are no windows in the line of sight of the spectrometer nor any other parts to scatter undesired radiation to the observing apparatus. The thicknesses of the disk-shaped carbon and beryllium scatterers used in this work were, respectively, 2.96 mm and 4.85 mm. The face areas of the scatterers were such that they occupied approximately the full cross section of the one-inch aluminum tube through the target axis.

The double spectrometer employed has been fully described[9] but it will be useful to emphasize again that by no possibility can its scales be in error by an amount comparable to the probable errors attached to the observations which follow, much less to the observed shift defects or differences between the measured shifts and those predicted by the Compton formula. The angular scale of the B crystal, a circle by Societe Genevoise, has been checked by intercomparison of its parts, by comparator observation of the linear motion of the end of a two-meter bar fixed to its turn-table, and by the observation of many well-known spectrum lines and limits. In a spectrometer of this type the A crystal is never required to rotate and we have made sure by optical lever observations that no rotations approaching a second of arc can, in fact, occur as the crystal is caused to execute its permissible motions.

The spectrometer was equipped with polished calcite crystals characterized by faces ten centimeters long and rocking curves 41 seconds in full width at half maximum. In the spectrometer system sensitivity was sacrificed to stability to such an extent that with the crystals operating at full aperture and the x-ray tube under a load of three to three and a half kw a single scattering observation required an exposure one minute in duration.

Experimental Procedure

Former shift measurements have as a rule been made with the strong $K\alpha$ doublets of the elements. Though the intensity available in this way is of great advantage, it is well known that modified $K\alpha$ spectra show little or no resolution, on account of the Doppler broadening of the lines, and this introduces an uncertainty into the shift determination, inasmuch as it must be measured between a single line and a pair. Though such a measurement could perhaps be successfully carried out, either by graphic resolu-

[8] Paul Kirkpatrick and P. A. Ross, Rev. Sci. Inst. **4**, 645 (1933).

[9] P. A. Ross, Rev. Sci. Inst. **3**, 253 (1932).

tion of the modified line or by location of the centroid of the unmodified, we have had reason to distrust these methods and have chosen to avoid this complication by the use of the much weaker β-line, which is, practically speaking, single and symmetrical.

All of our observations have been directed to the determination of wave-length shifts associated with a scattering angle of 90°. With the scatterer in a given position (not necessarily the precise position for ninety-degree scattering) we observe the magnitude of the shifts first with radiation emerging from one end of the tube, and then from the other (Fig. 1). Since the observing spectrometer is necessarily stationary, this is, of course, done by rotating the x-ray tube through 180° about a vertical axis passing through the scatterer, the exactitude of the angle of rotation being checked by observing a mirror on the x-ray tube through a telescope equipped with a Gauss eyepiece. The mean of these two shifts, after certain small corrections have been applied, is taken to be the shift associated with a scattering angle of 90°.

This conclusion is readily justified under the original Compton shift equation, which at worst is certainly an excellent approximation to the truth. For if $\Delta\lambda$ and $\Delta\lambda'$ are the shifts observed at the (unknown) supplementary angles φ and φ' we have by addition $\Delta\lambda+\Delta\lambda'=2h/mc$.

We recently proposed,[6] amending the Compton equation to read $\Delta\lambda=(h/mc)(1-\cos\varphi)-D\lambda^2$, a proposal to be more fully discussed in a later paragraph. It is readily verified that this expression similarly leads to the conclusion that the mean of the shifts for two supplementary angles is equal to the 90° shift.

The modified lines obtained show a broad base, sloping gradually up to a steeper peak. These observations were not well adapted to a study of the precise shapes of the modified lines because of the rather wide variability of scattering angle which was tolerated. We have observed, however, that the width and shape of the line, particularly the shape of the basal portion, vary with variation of the scattering substance, an expected result in consequence of the non-identical electron momentum distributions of the elements. This subject will be treated in a later paper.

Present interest centers in the upper, steeper portion of the modified line. Our shift measure-

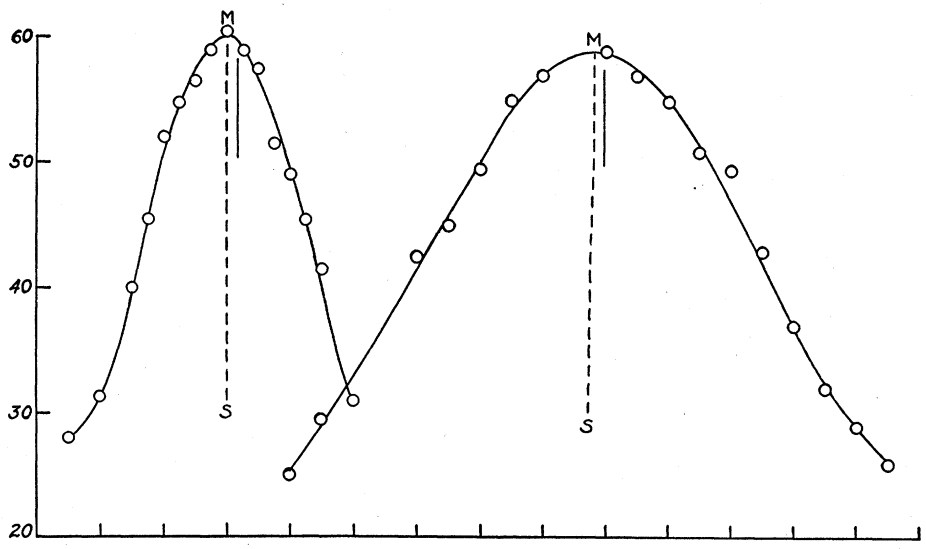

FIG. 2. Modified $K\beta$ of molybdenum, scattered by carbon. Ordinates are electrometer scale divisions per minute. Abscissas are angular settings of B crystal with reference to an arbitrary zero. The divisions marked off on this axis are at intervals of four minutes of arc. Angles of scattering for these two curves are supplementary, that for the left curve being about 64°. On this scale the unmodified Mo $K\beta$ would be about four minutes to the left of the axis of ordinates. Dashed lines are center lines of these curves. The parallel solid lines are the center lines which would be required by the Compton shift formula.

ments are measurements of the wave-length interval from the centroid of the unmodified $K\beta$ line to the *maximum* of the modified line. This maximum was found by locating midpoints at various heights and connecting them by a smooth line such as SM in Fig. 2, terminating in the maximum, M. In a large number of cases the line SM was found to show no measurable systematic inclination to right or left, so that the *maximum* practically means also the centroid of the upper portion of the modified line.

A number of preliminary curves were obtained with the scatterer placed rather accurately in the ninety-degree position, but since this is a position of low scattered intensity all final data were collected with the mean scattering angle equal to 64° or its supplement. No measurable difference between real 90° shifts and the corresponding mean shifts for mutually supplementary angles was observed.

Corrections

The most important correction which must be applied to the shifts as observed is that which compensates for the effect of scatterer thickness upon the mean angle of scattering. Due to absorption of the emergent scattered radiation within the scatterer the side of the scatterer which is away from the spectrometer is in a disadvantageous position as compared to the side toward that instrument, and as a result the *effective position* of the scatterer is not identical for the two supplementary angles of scattering, though the real position of the scatterer relative to the target remains unchanged. This means that the two *effective angles* of scattering are not accurately supplementary and that a correction for this inaccuracy must be calculated. To obtain the 90° shift in the case of a disk scatterer whose thickness is small in comparison to its diameter analysis shows that one must add to the mean of the wave-length shifts pertaining to the two supplementary angles of observation a small length δ given by

$$\delta=\frac{c\sin^2\varphi}{2\mu R}\left\{\frac{1}{\sec\varphi+1}\log\left[\frac{1+e^{-\mu X(\sec\varphi+1)}}{2}\right]-\frac{1}{\sec\varphi-1}\log\left[\frac{1+e^{-\mu X(\sec\varphi-1)}}{2}\right]\right\}.$$

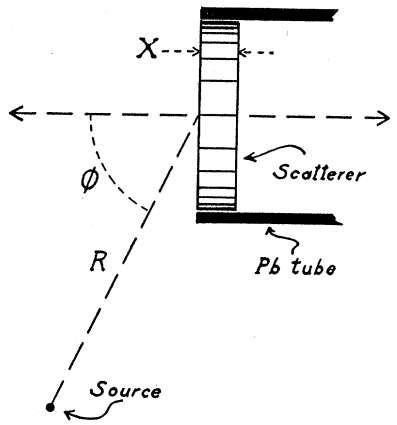

FIG. 3. Arrangement of scattering disk and source (not to scale). Quantities concerned in scattering angle corrections are illustrated.

In these equations c is the (approximate) 90° wave-length shift, and μ the mean absorption coefficient of the modified and unmodified radiation in the scatterer. The other symbols are defined by Fig. 3.

No x-ray spectrometer is uniformly sensitive to different wave-lengths, since crystal reflection and the absorption by windows, air and chamber gas exhibit wave-length variations. This total sensitivity variation distorts any spectral feature under observation, causing apparent shifts in the positions of lines and absorption limits. The shift of a narrow line may be so slight as to be unobservable but for lines having real widths as great as those of modified scattered lines the effect may not be dismissed without investigation.

Accordingly the variation of spectrometer sensitivity with wave-length was investigated by comparing the measured relative intensities of the K lines of certain elements with the real relative intensities given by Williams.[10] The sensitivity was found to increase slightly with wave-length, a result indicating incomplete absorption in the ionization chamber. From the observed sensitivity characteristics shift corrections applicable to the modified lines were computed.

The scattered radiation in emerging from the scatterer undergoes filtration which tends to suppress the long wave-length side of the modi-

[10] J. H. Williams, Phys. Rev. **44**, 146 (1933).

fied line and thus cause the observed maximum to occur at too small a wave-length. The small corrections required by this effect have been calculated and applied. It is unnecessary to correct for the line shifts caused by vertical divergence of rays passing through the spectrometer, since such shifts apply practically identically to modified and unmodified lines.

Experimental Results

Ring targets of molybdenum, silver and tin were used, and in each case scattering disks of carbon and beryllium were successively employed. With each of the six combinations the contour of the modified $K\beta$ line was traced out with the spectrometer five or six times, using a scattering angle of about 64°, and again with the supplement of this angle. Thus for each scatterer and radiation a value of the ninety-degree shift is obtained which derives from ten or more individual shift measurements. All of these data, together with the corrections discussed above, are summarized in Table I.

The superiority of the carbon data over the best obtainable with beryllium was evident throughout the investigation. Though the density of scattering electrons in the two substances was approximately the same the beryllium was contaminated by a small amount of some heavy impurity which was sufficient to give the specimen a measured linear absorption coefficient three times as great as that of the carbon. In spite of this difficulty it was deemed important to collect such beryllium data as could be had, in order to compare the magnitudes of shifts produced by different scattering atoms.

Discussion

The most striking feature of the data in Table I is the fact that all the ninety-degree shifts are less than the Compton value, h/mc, by amounts much too great to be attributable to experimental error. In the case of Mo $K\beta$ scattered by carbon this discrepancy attains the high value of 2.4 percent. This is in agreement with earlier results,[11] announced at the 188th meeting of the American Physical Society. We have made over a hundred measurements of this shift within the past two years, using various wave-lengths and angles, and with scatterers differing in material, size and shape. In all of this work the general conclusion that the ninety-degree shift is measurably less than h/mc has been uniformly confirmed. It should perhaps be recorded that all of these measurements have been performed with the same apparatus.

In our revision[6] of the shift equation of Compton the binding energy E of the scattering electrons was considered and the scattering process was assumed to be of finite duration. According to the revised equation $\Delta\lambda=(h/mc)(1-\cos\varphi)-\lambda^2kE/hc$ where k is a constant of the order of magnitude of unity, whose precise value cannot be calculated by the elementary methods upon which the derivation was based. So long as we are in ignorance of k it is not possible to achieve a complete quantitative comparison of theory with experiment, though general conclusions may be drawn regarding the theoretical and experimental variation of the ninety-degree shift with wave-length and binding energy. At ninety degrees the equation above requires $\Delta\lambda_{90}=h/mc-D\lambda^2$, which means that in Fig. 4 the observed points should fall upon a straight line of negative slope having an intercept at h/mc on the axis representing shifts. It is seen that the beryllium data, though scattered, show a definite wave-length variation of this sort, while the carbon points lie very close indeed to a line of the required type. Furthermore the carbon shifts differ from h/mc in all cases more than do the shifts of beryllium, a fact which may be reasonably interpreted along the lines of the present theory as a result of the greater binding energies characterizing the electrons of carbon.

It is unprofitable to press a classical or semi-classical theory of atomic processes beyond a certain point and it is particularly unnecessary in this case since the matters under discussion are treated from a more fundamental standpoint in the following paper which Professor Felix Bloch, at our suggestion, has been so kind as to prepare. As he shows, it is possible to deduce a shift equation without ambiguity and without any arbitrarily adjustable constants. His results for the shift of the maximum of the modified line

[11] P. A. Ross and Paul Kirkpatrick, Phys. Rev. **45**, 135 (1934).

TABLE I. *Summary of data and corrections.*

Radiation	λ (X.U.)	Scatterer	*B* crystal shift angle	$\Delta\lambda_{90}$ uncorrected (X.U.)	Corrections: Scatterer thickness (additive)	Corrections: Spectrometer sensitivity (subtractive)	Corrections: Scatterer filtering (additive)	$\Delta\lambda_{90}$ corrected (X.U.)
Sn $K\beta$	435.	carbon	27.16′	23.87	0.03	0.02	0.00	23.88±0.03
" "	435.	beryllium	27.29′	23.98	0.16	0.02	0.01	24.13±0.06
Ag $K\beta$	496.	carbon	27.09′	23.78	0.03	0.02	0.00	23.79±0.03
" "	496.	beryllium	27.02′	23.72	0.19	0.02	0.02	23.91±0.06
Mo $K\beta$	631.	carbon	26.87′	23.52	0.05	0.02	0.01	23.56±0.03
" "	631.	beryllium	27.03′	23.66	0.24	0.02	0.02	23.90±0.06

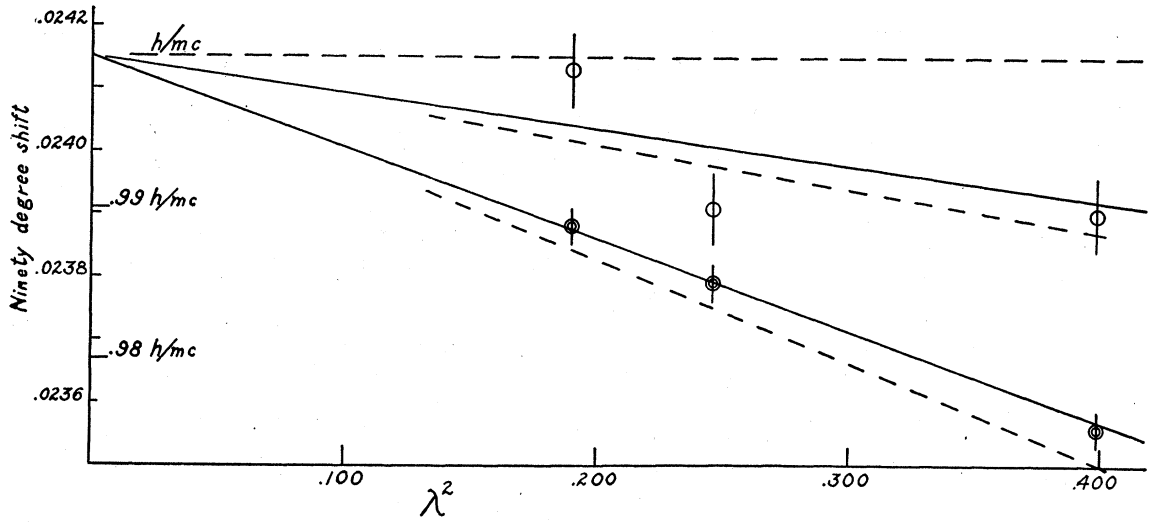

FIG. 4. Wave-length shift in Angstroms for ninety-degree scattering *vs.* square of incident wave-length in Angstroms. Single circles represent observed scattering by beryllium; double circles by carbon. Solid lines are the straight lines which best fit the data and possess the intercept h/mc. Dotted lines indicate the requirements of Bloch's theory.

in ninety-degree scattering are given by the dotted lines in Fig. 4. The agreement between experiment and theory, though not perfect, is most encouraging. Further experiments, with pure beryllium and with many other scatterers, are now in preparation.

In the problem of the determination of fundamental physical constants it has been the practice to accept the measured value of any ninety-degree shift as a determination of h/mc. It is now seen that conclusions so drawn must be erroneous, and that h/mc is to be determined by extrapolating observed shift data to zero wave-length. The carbon data of Fig. 4 when treated in this way yield a value $h/mc = 0.02418 \pm 0.00004$. The precision of this determination will be greatly improved by the use of a wider range of wave-lengths.

It remains to acknowledge our appreciation to the National Research Council for a grant-in-aid which made possible the purchase of apparatus essential to this investigation.