JULY 15, 1938 PHYSICAL REVIEW VOLUME 54

The Silver L Series X-Ray Spectrum: Line Widths, Wave-Lengths, Relative Intensities, Satellites, and Widths of Energy Levels

LYMAN G. PARRATT
Cornell University, Ithaca, New York

(Received April 16, 1938)

With a new two-crystal vacuum spectrometer a systematic and precise study of 36 L series emission lines of silver has been made which includes measurements of wave-lengths, relative intensities, line widths and indices of asymmetry. These lines include 21 satellite lines. The contours of the three L absorption edges of silver were also recorded. From these data have been determined the widths of all the energy levels for single ionization of silver. From the widths of satellite lines are discussed the widths of certain states of double ionization.

INTRODUCTION

RECENT developments in x-ray spectroscopy are the quantitative correlations of (1) widths of x-ray emission lines and widths of absorption limits; (2) widths of "parent" lines and relative intensities of "satellite" lines; and (3) relative intensities, widths and wave-length positions of satellites. These are separate aspects of the problem of double (or multiple) ionization. The importance of multiple ionization was realized many years ago in connection with the Auger effect, with satellites and with certain fine structure in absorption edges, but only recently has the synthetic development of the physical concepts of the several phenomena reached the point where interrelating generalizations can be seen.[1]

The present paper reports the first systematic investigation of a complete L series spectrum with an instrument, a two-crystal vacuum spectrometer, having sufficiently high resolving power to measure the pertinent spectral properties. This study of 36 L series emission lines of silver ($Z=47$) includes measurements of wave-lengths, relative intensities, line widths and indices of asymmetry. These lines include 21 satellite lines. The contours of the three L absorption edges of silver were also recorded. From these data have been determined the widths of all the energy levels for single ionization (and in some cases for double ionization) of silver in the manner followed by Richtmyer, Barnes and Ramberg[2] in the case of gold. The contours of the absorption edges are found to abound with secondary structure and, although too complex to allow a simple direct measurement of energy level widths, promise exciting possibilities in quantitative studies of the Brillouin zones or crystal lattice energy levels in metallic silver or of energy levels in nongaseous substances in general.

EXPERIMENTAL

Spectrometer

The new two-crystal vacuum spectrometer differs but little in general design from its prototype.[3] The inside diameter of the tank has been increased from 50 to 60 cm; the distance between the crystals from 12 to 13.5 cm.

The ionization chamber, made of steel, is 3.5 cm in diameter and 9 cm in length; and has a window in the rear to allow the exit of unabsorbed x-rays. The collector rod has been extended to form a loop around the entrance window so as to collect more of the ions before recombination in the fore part of the chamber. Thin Cellophane (or Kodapak, less absorbing but also less tough), 0.5 mil thick, is used as the entrance window and is made electrically conducting by a negligibly thin aluminum foil placed on the window's inside. A conducting window is essential in facilitating saturation of the ion currents produced by radiations of widely differing intensities or of widely differing penetrations in the gas in the chamber.

To provide easy control of the gas pressure in the ion chamber and to allow the use of a very thin window that will support but a fraction of an atmosphere pressure, the gas inlet to the ion

---

[1] For recent papers illustrating this progress see F. K. Richtmyer, Rev. Mod. Phys. **9**, 391 (1937) and references.

[2] F. K. Richtmyer, S. W. Barnes and E. G. Ramberg, Phys. Rev. **46**, 843 (1934).

[3] L. G. Parratt, Phys. Rev. **41**, 553 (1932); Rev. Sci. Inst. **5**, 395 (1934) and **6**, 387 (1935).

chamber is connected by a flexible tube through the base plate (supporting the spectrometer) to the outside of the tank. Trouble with residual ionization (α-particles, etc.) is materially reduced by operating with a minimum gas pressure in the chamber.

The ionization currents were amplified with a WE-D96475 electrometer tube mounted adjacent to the ion chamber inside of the evacuated tank. The Barth[4] circuit was used with a maximum sensitivity of about 200,000 mm/volt/meter. Any one of five high resistors, in about equal and known steps from 10^9 to 10^{12} ohms, could be placed in the control-grid circuit by a switching device manipulated outside of the tank.

Linearity of the recording system was certified by comparisons of the absorption coefficient of silver for $\mathrm{Ag}L\alpha_1$ radiation for each of two thicknesses of silver foils which reduced the ionization currents by factors of about 2 and 900, respectively. The two coefficients agreed within the experimental error of about 2 percent.

Crystals

Unfortunately the calcite crystals A_4B_4, exhaustively studied[5] some time ago, have deteriorated, spectrometrically speaking, during the intervening time. The reflecting characteristics of these crystals, cleaved and etched, have changed in $2\frac{1}{2}$ years as shown in Table I. The beginning of this change was suspected earlier.[5] These crystals were kept in a vacuum about ten months and were exposed to air in the laboratory about twenty months. Fortunately, repeated etching processes were successful in restoring the crystals to their earlier degree of perfection (or even slightly better, as shown in Table I) and so, as used in this study, the crystals may be called perfect crystals[5] of class I.

TABLE I. *Change with time in reflectivities of etched calcite crystals. Measured with* Mo$K\alpha$ *radiation, wave-length 0.71*A.

	1935	1937	1937 After Re-etching
(1, −1) full width	5.2″	8″	5.0″
(1, +1) full width	21.0″	27″	21.0″
Percent reflection in first order	66	40	67

X-ray tube

The specially designed x-ray tube is clamped in a vertical position onto the side of the tank. Through a sylphon bellows at each end of the tube, adjustments can be made to place either the filament or the target at any point in the space near the center of the tube. These adjustments greatly facilitate regulation of the shape and size of the focal spot, allow the best part of the target surface (important with powder targets) to be used as the focal spot, and permit easy alignment of the focal spot and slit. The surface of the target is inclined 30 degrees with respect to the path of the central ray to the first crystal.

To reduce the intolerable tungsten condensate on the target a shielded filament similar in design to the one described by Dershem[6] was found to work satisfactorily when the excessive heat produced by radiation from the filament was adequately dissipated. The grid-wire in this unit was found to be a very insensitive control and was dispensed with entirely.[7] The type of filament unit found most satisfactory[8] consisted of two cylindrical spiral filaments, about 20 turns of 5 to 7 mil tungsten, $\frac{1}{16}''$ in diameter and $\frac{1}{2}''$ long, connected in series, placed behind and offset on either side of a rectangular hole, $\frac{3}{16}''\times\frac{1}{2}''$, cut in the blind end of a steel tube $\frac{3}{4}''$ in diameter. With a uniform focal spot 7×5 mm, as used in the present study, this unit delivered more than 100 ma at 15 kv, although the steel shield was then red hot. To avoid this heating, which, for steady operation of the tube, requires an almost impractical outgasing process, oxide-coated filaments were tried but their emission was too spotty, the focal spot was not uniform, and there was a high probability of burning a small hole through the target. Carefully activated thoriated tungsten filaments served very well as long as a good vacuum was maintained. Adequate water-cooling of the shield is a better solution.

Targets

Several specimens of silver were used as targets to rule out spurious lines due to impurities. Gold

---

[4] D. B. Penick, Rev. Sci. Inst. **6**, 115 (1935).

[5] L. G. Parratt, Rev. Sci. Inst. **6**, 387 (1935) and L. G. Parratt and F. Miller, Jr., Phys. Rev. **49**, 280 (1936).

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

[7] One of the requirements of Dershem's filament design was the elimination of light direct from the filament and scattered from the target. In satisfying this requirement the grid-wire and deflecting shield serve an important function.

[8] Pierce, Olson and MacMillan, Rev. Sci. Inst. **8**, 145 (1937), describe another shielded filament unit, similar to the present one.

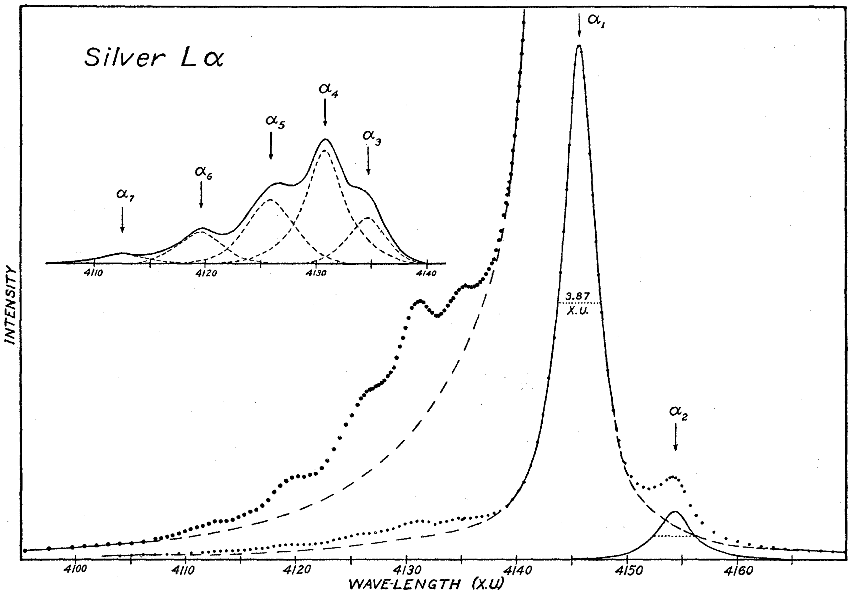

FIG. 1. Intensity plot (ionization recordings) of the Ag*L*α region. The upper satellite region, on the short wave-length side of α_1, is replotted with the intensity scale increased 6.3 times. Five component satellite lines have been sketched in.

was chosen as the target for producing the continuous radiation because of freedom from the *M* series lines in the spectrum range studied and because of the practical difficulties in making satisfactory targets of higher elements.

The tube voltage[9] was maintained at 15 kv for the emission spectrum and at 12 kv for the absorption curves. The lower voltage for the continuous radiation was used (1) to prevent gold *L* series lines from being excited and coming through in third-order reflection, and (2) as a practical compromise between the intensity of the continuous radiation in first order and the unwanted continuous radiation in second-order reflection.[10]

Working x-ray intensity

The peak intensity of the $L\alpha_1$ line at 4.15A with the tube operating at 15 kv and 40 ma produced an ionization current of 6×10^{-13} ampere, equivalent to a full sensitivity scale deflection of 12,000 cm.

The intensity of the continuous radiation at 3.9A with the tube operating at 12 kv and 60 ma produced an ionization current of 1.2×10^{-14} ampere, a full sensitivity scale deflection of 250 cm, which could be read and repeated with a precision of about one percent.

MEASUREMENTS

Ionization curves

Figures 1 and 2 are reproductions of the α and the β lines of the observed Ag(47) *L* series spectrum. Fig. 2 is a composite of several overlapping sections recorded at different "sittings." The lower curve in Fig. 2 is plotted to an intensity scale magnified 15 times with respect to the scale in the upper curve. The accuracy with which the data were recorded is indicated by the consistency of the points on these curves.

In taking these data the base line or zero in-

---

[9] See L. G. Parratt, Phys. Rev. **49**, 133 (1936) for description of the voltage supply.

[10] The ratio of the coefficients of reflection of each of the two crystals for reflection in first- and in second-order aids in minimizing the intensity of the second-order radiation. This ratio, 16 to 1 for the second crystal as interpolated from measurements by Parratt and Miller, reference 5, gives an effective ratio of about $1.5\times(16)^2$ or 400 for the coefficient of reflection of *both* crystals (400 in angular measure or about 50 in wave-length measure). The factor 1.5 is designed to take care (approximately) of the polarization of the beam upon reflection at the first crystal. The differential absorption of the first- and second-order beams is a hinderance in this minimization of second-order intensity.

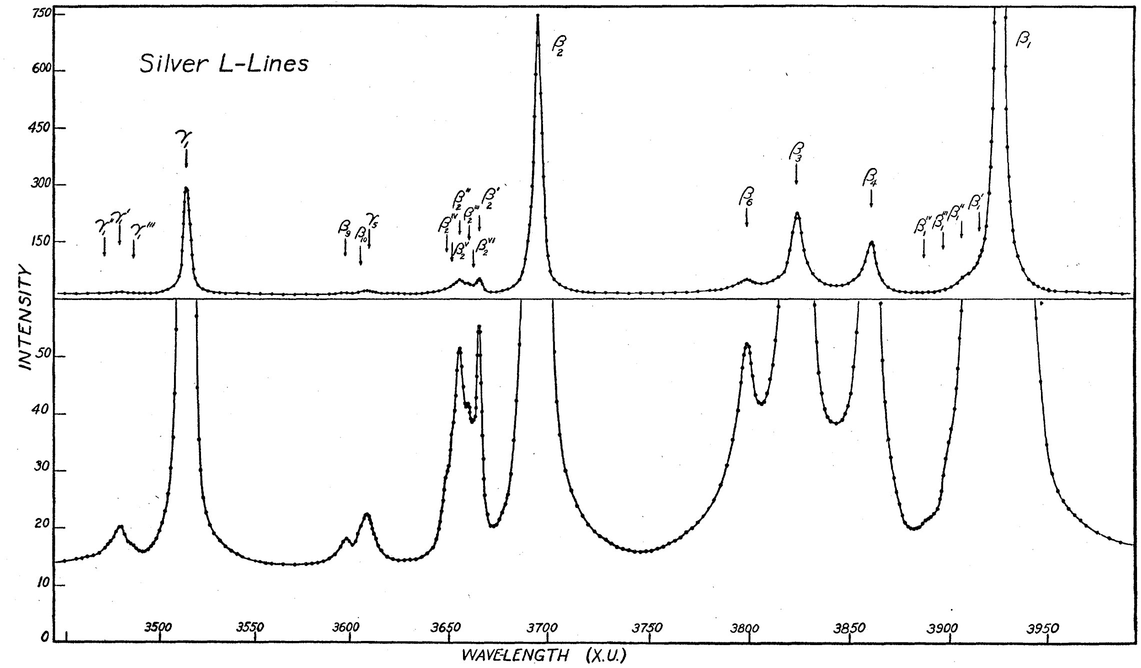

FIG. 2. Intensity plot (ionization recordings) of the Ag$L\beta$ region. The lower curve is plotted to an intensity scale 15 times the scale of the upper curve. The accuracy in measuring the various properties of most of these lines is limited not by the low intensity nor by the intensity readings but by the arbitrary resolution into component structure. The overlapping of these lines in inherent and cannot be reduced appreciably by increasing the resolving power of the (two-crystal) spectrometer with which their contours are recorded. The peak of the β_1 line is 4.8 times as high as the β_2 peak; the peak of the α_1 line, the strongest line of the series, is 8.25 times as high as the β_2 peak.

tensity was determined many times in the progress of each curve by placing temporarily a thick lead absorber in the beam. This procedure reduces the danger in the assumption of no "zero drift" or of uniform "zero drift." Also, this use of a complete absorber obviates the (all-too-frequent) interpolation to get the base-line between the "ends" or minima of such curves. Such an interpolation desirably ignores the background of continuous and of scattered radiation but also undesirably "fixes" arbitrarily the height and wave-length extent of each "line." In measuring line widths and relative intensities it is necessary, however, to discount the undesired background, especially for the weaker lines, such as η or β_6, β_9 or γ_5 (see the lower plot of Fig. 2). As yet we are forced to an arbitrary distinction between true line and background from the observed contours; a satisfying distinction can be made only when the complete intensity plot, including true line and background, is before us.

Figure 3 is the observed contour of the $\gamma_{2,\,3}$ lines. This contour illustrates a major difficulty in studies of this kind: The line widths are so great that close-lying lines seriously overlap one another and defy a unique resolution into components. An attempt at such a resolution is, of course, imperative in making a measurement of relative intensity, line width, shape or wave-length position. This overlapping is characteristic of the lines themselves and *cannot be reduced* appreciably by increasing the resolving power of the spectrometer.

The difficulty in resolving the α structure into component lines has been discussed in an earlier paper[11] with the conclusion that, in the analysis of contours recorded with practically infinite instrumental resolving power, we must resort to an arbitrary "reasonable" resolution, determined by the observer's best judgment.

Another poignant example of arbitrary but "reasonable" resolution is illustrated by the $L\beta_2$ satellite contour and components, Fig. 4.

The observed contour of the L_{III} absorption limit of silver, shown in Fig. 5, is the average of

---

[11] L. G. Parratt, Phys. Rev. 50, 598 (1936).

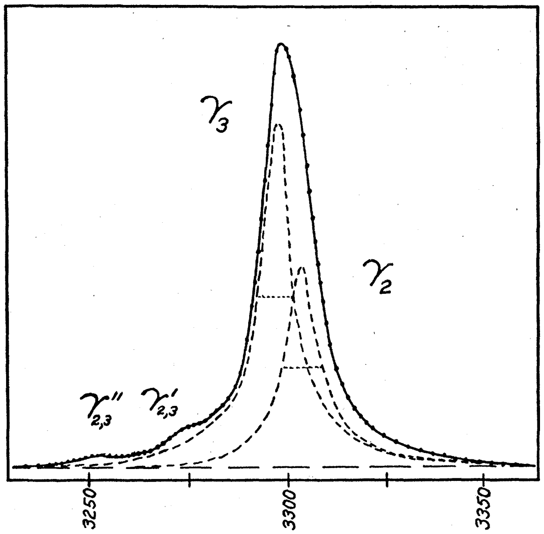

FIG. 3. The observed contour of the Ag$L\gamma_{2,3}$ lines illustrates the difficulty and the arbitrariness of the necessary resolution into components.

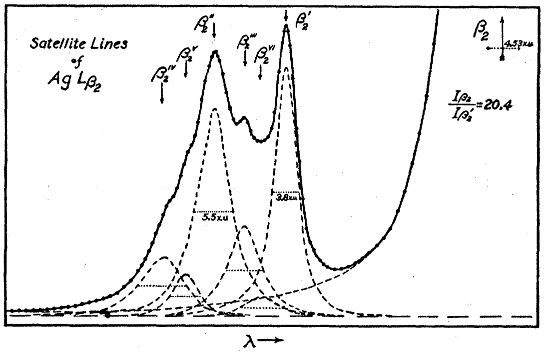

FIG. 4. The observed contour of the Ag$L\beta_2$ satellite structure is resolved into six components. Theory indicates that forty components of varying relative intensities and mostly unresolved should be present. The satellite line $L\beta_2'$ is less wide, 3.8 x.u. (3.5 x.u. corrected), than the "parent" line $L\beta_2$, 4.53 x.u. (4.1 x.u. corrected); this is the first satellite (or double ionization) line to be so reported. See text.

six curves taken with four different Ag foils. The average thickness of the absorbing foils was about 12,000A, which is the calculated optimum thickness, i.e., the thickness which gives the maximum relative change in the intensity at the L_{III} edge, when the absorption coefficients listed in the *Handbook of Chemistry and Physics*[12] are used.

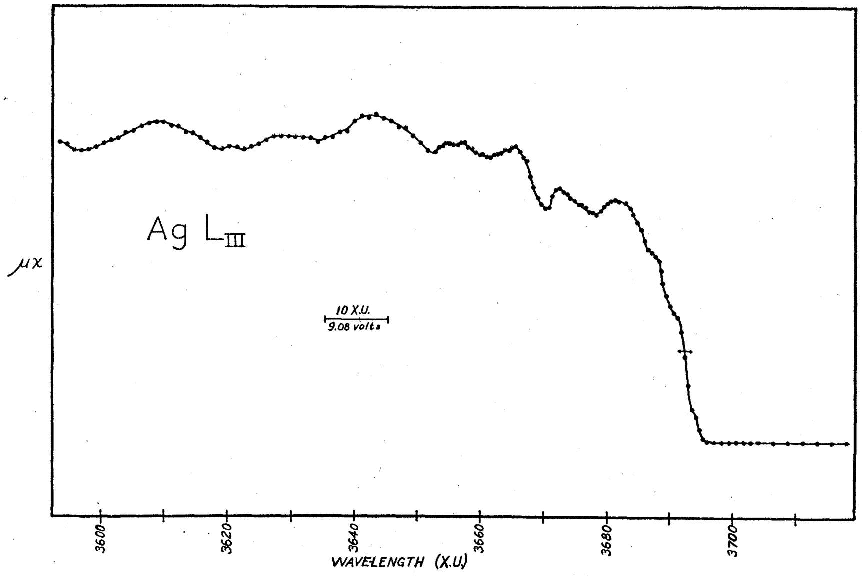

FIG. 5. The absorption (coefficient) of silver in the wave-length region of the AgL_{III} absorpton limit. In addition to the main absorption edge are found a series of absorption maxima. These maxima represent resonance absorption lines (or zones) corresponding to the ejection of the $(2p_{3/2})$ electron to outer unfilled energy levels. Atomic or optical levels are engaged in the resonance lines lying within about 9 electron volts (ionization potential of Cd(48), $Z=47+1$) from the main edge; crystal lattice energy levels (or zones) are involved in the more removed maxima. The width of the Ag$L\alpha_1$ line is indicated by the length of the arrow on the main edge: The width of the L_{III} energy state must be less than the length of this arrow.

---

[12] *Handbook of Chemistry and Physics*, 19th edition, p. 1381.

Except in studying the details in small wave-length ranges, the large wave-length extent of these curves required that both crystals, the positions of the x-ray tube and of the ion chamber *all* be adjusted simultaneously as the recordings were in progress. In this way, the same effective region of each crystal was used in reflection, and proper alignment of the focal spot, crystals and ion chamber was maintained at all times.

Correction for resolving power

Since the widths of L series lines are relatively great (2 to 10 times as great as of K series lines of the same wave-length) the utmost in resolving power in the spectrometer (using special quartz crystals or higher orders of reflection[5]) is not necessary; in fact, is a detriment in recording *weak* lines. For this work the numerical resolving power ($\lambda/d\lambda$) was about 11,000 to 12,000: The $d\lambda$ interval in first-order reflection was about equal to 1/10 of the width, 3.45 x.u., of the narrowest observed line, β_1; or about 1/50 of the widest line, l, 22.2 x.u.

The correction to be applied to observed non-overlapping lines in obtaining the true line contours, for purposes of measuring true line widths and relative intensities, is perhaps small with the present resolving power but is much greater than the observational error in recording the curves. This statement is not true in the cases of very faint or badly overlapped lines. The correction formula previously proposed[5] in terms of the (1, −1) and (1, +1) widths in x.u.

$$W_T = W_0 - 2.9W_c^{1.7} \tag{1}$$

at half-maximum intensity, has been applied to the measured line widths in a somewhat arbitrary manner; the full correction was applied in cases of distinctly separate or naturally resolved lines, e.g., α_1 or β_1, and an arbitrary fraction of the full correction was applied in cases of overlapping lines, e.g., α_2, β_2'' or γ_3. It is obvious that the same or full magnitude of correction, Eq. (1), cannot be applied to these two types of lines without introducing another appreciable error in the overlapping lines. To correct ***properly***, one must very arduously operate on the observed contour instead of on the resolved components. An approximate method for doing this has been proposed by Spencer and this double inverse graphical procedure has been used as a guide[13] in the corrections made in the present analyses for line widths and for relative intensities.

WAVE-LENGTHS

The writer's spectrometer is not capable of absolute wave-length measurements but is capable of measuring accurately small wave-length intervals. The wave-lengths of the $L\alpha_1$, β_1 and γ_1 lines of Ag(47) given by Haglund[14] were used as standards. Listed in Table II are wave-length intervals and wave-lengths of lines referred to Haglund's measurements as indicated. These values are believed to be more accurate than wave-lengths heretofore reported for the AgL series lines. Unfortunately, the l and η lines are too far removed from the α_1 line to be included with the new data in this table.

The γ_5, β_9 and β_{10} region requires comment. The observed contour of this region includes two well defined maxima, Fig. 2, and a slight irregularity, indicating a third line, between them. Two interpretations of this contour are possible: (1) we may heed the slight irregularity and say three lines are present; or (2) we may conclude that only two lines are observed, say the β_9 and β_{10} or the β_9 and γ_5. In favor of the first interpretation, as herein adopted, are four arguments. First, the wave-length interval between β_9 and β_{10} should be the same as the interval between α_1 and α_2; both intervals are equal to the separation of the M_{IV} and M_V energy levels. The separation of the observed maxima, perhaps the β_9 and β_{10} lines, is 11.9 x.u. whereas the $\alpha_1 \rightarrow \alpha_2$ separation is but 8.5 x.u. Second, the width of each of just two components is greater than one might reasonably expect for the β_9 line and for either the β_{10} or γ_5 line according to a criterion to be discussed later. Third, the Burger-Dorgelo sum rules for relative intensities predict an intensity ratio of 1 to 0.67 for β_9 to β_{10}, whereas the observed intensity ratio of the two lines is 1 to 2.9. The sum rules also predict an intensity for γ_5 equal to one-half of the intensity of β_6 or a γ_5 intensity 0.7 of the in-

---

[13] R. C. Spencer, Phys. Rev. **38**, 618 (1931), and L. G. Parratt, Phys. Rev. **49**, 138 (1936).

[14] P. Haglund, Zeits. f. Physik **84**, 248 (1933). See also A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Co., Inc., 1935), p. 786, and M. Siegbahn, *Spektroskopie der Röntgenstrahlen*, second edition (Julius Springer 1931), p. 228.

tensity of the higher peak of the contour in question. Fourth, if we derive from the combination principle and the energy level diagram the wave-length of $\gamma_5(L_{II}N_I)$ we equate $1/\gamma_5=(1/\beta_1)+(1/\beta_6)-(1/\alpha_2)$ and obtain $\gamma_5=3608.5$ x.u., when the wave-lengths in Table II are used. In a sense, the consideration of such arguments partially defeats the purpose of the experiments which are carried out to obtain data *from* which, rather than *to* which, such arguments may be made, but we must concern ourselves with the identification and the assignment of names to the observed lines or components.

The wave-lengths of the lines β_9 and β_{10} are radically different from Coster's (see Table II). In order to make doubly sure of the present wave-length scale, the position of Sn$L\alpha_1$, 3592.57 x.u. from Siegbahn's tables, was measured and checked as a secondary standard.[15]

TABLE II. *Wave-lengths of peaks of lines of the L series spectrum of silver* ($Z=47$). *The wave-lengths of the three lines* γ_1, β_1 *and* α_1 *as measured by Haglund are used here as standards to which all the other lines are referred. For ready comparison the satellite measurements by the Richtmyers have been referred to the present values as standards instead of to Coster's values.*

LINE	TRANSITION	SEPARATION (SECONDS OF ARC)	SEPARATION (X.U.)	WAVE-LENGTH (X.U.)	PREVIOUS MEASUREMENTS (X.U.)	OBSERVER*
$\gamma_{2,3}''$	Satellite	10870	264.3	3251.15	—	
$\gamma_{2,3}'$	"	10000	244.0	3271.45	3270	D
γ_3	L_IN_{III}	8920	215.8	3299.65	—	
$\gamma_{2,3}$	—	8870	214.4	3301.05	3299.8	C
γ_2	L_IN_{II}	8680	210.0	3305.45	—	
γ_1'''	Satellite	1790	42.9	3472.55	—	
γ_1'	"	1455	34.85	3480.60	3480	D
γ_1''	"	1130	27.1	3488.37	—	
γ_1	$L_{II}N_{IV}$	0	0	[3515.45]	3514.9	H_j, C
β_9	L_IM_V	3410	80.9	3596.35	3620	C
β_{10}	L_IM_{IV}	3765	89.3	3604.8	3630	C
γ_5	$L_{II}N_I$	3930	93.2	3608.6	3607.3	C
β_2^{iv}	Satellite	5626.5	133.2	3648.65	3648.2	R
β_2^{v}	"	5763	137.4	3652.9	—	
β_2''	"	5928.5	140.3	3655.75	3655.6	R
β_2'''	"	6110	144.6	3660.0	3660.4	R
β_2^{vi}	"	6201.5	146.6	3662.1	—	
β_2'	"	6355	150.9	3666.35	3665.4	R
$\beta_2^{(a)}$	"	—	—	—	3691.0	R
β_2	$L_{III}N_V$	7635	180.05	3695.50	3695.60	H
β_6	$L_{III}N_I$	12170	284.45	3799.90	3798.6	C
β_3	L_IM_{III}	4515	101.5	3825.00	3824.5	H_j, C
β_4	L_IM_{II}	2870	64.4	3862.10	3861.1	H_j, C
β_1^{iv}	Satellite	1560	33.5	3893.0	3893.4	R
β_1'''	"	1250	27.0	3899.5	3899.5	R
β_1''	"	880	19.0	3907.5	3907.0	R
β_1'	"	510	11.0	3915.5	3914.9	R
β_1	$L_{II}M_{IV}$	0	0	[3926.50]	3926.6	H_j, C
α_7	Satellite	1587	34.15	4111.60	4112.65	R
α_6	"	1203	25.85	4119.90	4119.45	R
α_5	"	915	19.6	4126.15	4125.75	R
α_4	"	690	14.75	4131.00	4130.75	R
α_3	"	510	10.9	4134.85	4135.05	R
α_1	$L_{III}M_V$	0	0	[4145.75]	4145.6	H_j, C
α_2	$L_{III}M_{IV}$	397	8.48	4154.25	4153.8	H_j, C
η	$L_{II}M_I$	—	—	—	4410.1	C
l	$L_{III}M_I$	—	—	—	4697.6	C

* D = Druyvesteyn, 1928. Siegbahn, reference 14.
C = Coster, 1922. Siegbahn, reference 14.
H_j = Hjalmar, 1921. Siegbahn, reference 14.
R = Richtmyer and Richtmyer, 1929. Reference 17.
H = Haglund, 1933. Reference 14.

---

[15] The wave-length of Sn$L\alpha_1$ cannot be checked perfectly because of the discrepancies in the variously reported wave-lengths. We may refer the position of the Sn$L\alpha_1$ line to the wave-length of the intense and therefore easily measured Ag$L\beta_2$ line. The present observed separation of these two lines is 102 x.u. If we use Hjalmer's λ for Ag$L\beta_2$, 3693.8 x.u., we get 3591.8 x.u. for the λ of Sn$L\alpha_1$; if we use the present value for Ag$L\beta_2$, 3695.50 x.u., we get 3593.5 x.u. for Sn$L\alpha_1$. The two values thus obtained for the Sn line straddle the latest value given in Siegbahn's tables, 3592.57 x.u.,

Satellite lines

The $L\beta_2$ satellite lines also deserve further comment. Six β_2 satellites have been drawn under the observed contour of Fig. 4. Five of these correspond either to observed peaks or to observed irregularities of slope in the contour. The sixth, $\beta_2{}^{\mathrm{vi}}$, is not observationally necessary until we adopt the criteria of (at least fair) symmetry and reasonableness of shape of the component lines. If we do not adopt such criteria we are not allowed to measure, or even to speak of, any of the individual components of such a group. Indeed, the assumption of six $L\beta_2$ satellite components is ultra-conservative in view of recent trends in theory: Richtmyer and Ramberg[16] predict forty separate components in this satellite group for gold, the transition $(2p3d\rightarrow 4d3d)$.

The satellite line $L\beta_2{}^{(\mathrm{a})}$, at 3691.0 x.u. according to a measurement with the photographic method by Richtmyer and Richtmyer,[17] is not included in the present investigation. This is not a denial of the real existence of this line, but indicates, rather, an unwillingness on the writer's part to break up the extreme intimacy of $\beta_2{}^{(\mathrm{a})}$ and β_2.[18] This may be a case in which the technique of exposure (or overexposure) of a photographic plate may bring out for wave-length determination a faint line which is too faint, relative to an intense or a rapidly changing background (the side of a strong line), to show itself distinctly in a *linear* intensity plot. This possible advantage of the photographic method, notwithstanding its inferior resolving power, when in careful hands, has been anticipated before,[19] and, in a comparison of methods, is of considerable significance.

The γ_1 satellite contour is observed to be complex also, and the γ_1'' component is included mainly on the belief that the γ_1' component should have fair symmetry and a reasonable shape.

Two satellites accompanying the $\gamma_{2,\,3}$ lines are recognized in this study but there are indications that more than two components really exist.

RELATIVE INTENSITIES

To obtain transition probabilities from the observed relative intensities many troublesome corrections must be made,[20] such as corrections for absorption in the target, in the windows, in the air path, and in the ionization chamber; for variations in the coefficient of reflection of the crystal or crystals; and for ionization probabilities (which include the tube voltage). One correction which seems to have escaped adequate discussion in the literature so far and which is apt to be larger than some of those listed above is the correction for the resolving power of the spectrometer.

The relative intensity of two lines is defined as the ratio of the energy or power contained in one line with respect to that contained in the other line. This definition is subject to *two* experimental applications. In the first application the relative intensity is the ratio of the *maximum ordinates* of the two lines whose contours are recorded with a spectrograph or a spectrometer of *low resolving power*, an instrument whose effective $d\lambda$ interval or "spectral window" is many times greater (or wider) than the wave-length extent (or width) of each of the two lines being measured. In the second application relative intensity is the ratio of *areas* contained under the contours (plots of intensity *vs.* frequency) of the two lines when recorded with an instrument of infinite or, in practice, *very high resolving power*. In using an

---

reported by Wennerlöf. Hjalmer's value for Sn$L\alpha$ is 3592.2. These discrepancies, however, are too small to account for the 20 x.u. difference between the present wave-lengths and Coster's values for γ_5, β_9 and β_{10}.

[16] F. K. Richtmyer and E. G. Ramberg, Phys. Rev. **51**, 925 (1937).

[17] F. K. Richtmyer and R. D. Richtmyer, Phys. Rev. **34**, 574 (1929).

[18] It might be argued that additional component lines *should* exist on the short wave-length side of β_2 because of transitions between the L_{III} level and the levels just beyond the N_V level. Such lattice levels and their energy separations are shown in the absorption curve of Fig. 5. It is difficult to estimate the intensities one might expect for emission lines from these levels (excited states) but the fact that β_2 shows no especially peculiar shape between its peak and the β_2' satellite indicates that the intensities are low. (Part of the *width* of β_2 may be due to transitions from these levels in case the levels form an effective continuum.) However, an interpretation of this character for $\beta_2{}^{(\mathrm{a})}$ is, perhaps, not unreasonable.

[19] Compare, for example, the photographic and ionization recordings of identical spectral regions (1) of M. V. Dolejšek, Comptes rendus **174**, 441 (1922), and of L. G. Parratt, Phys. Rev. **49**, 502 (1936), (2) of M. H. Hulubei, Comptes rendus **201**, 544 (1935) and of C. H. Shaw and L. G. Parratt, Phys. Rev. **50**, 1006 (1936), (3) of F. K. and R. D. Richtmyer, Phys. Rev. **34**, 574 (1929) and of Fig. 1 of the present report, and (4) of A. W. Pearsall, Phys. Rev. **46**, 694 (1934) and of Fig. 4 of the present report.

[20] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Co., 1935), p. 652.

instrument having a spectral window between these extremes, one must tackle the difficult task of correcting the observed contours.

It is not generally feasible to apply a low resolving power instrument to accurate relative intensity measurements because so few x-ray lines appear as single or non-overlapping lines. In the spectral region of Figs. 1 or 2, for example, it is difficult to choose a spectral window of the proper extent to include all of one and only one line with an intensity uncertainty of less than, say, a few percent. With the assumptions that, for a given window position, the width of the window is properly chosen to include *all* of one line and *none* of other lines, or with an attempt to correct adequately when the assumption is not valid, the magnitude of the attending error in the relative intensity measurement is dependent upon the complexity of the spectral region being studied. Uncertainties from this cause may be as great as *several hundred percent* in the intensity ratios of faint lines close to a strong line, as the $L\alpha_1\alpha_2$ doublet, or as satellite and "parent" lines.

Investigators have appreciated the need for instruments of higher resolving power in studying overlapping multiplets, but, in using such instruments, have often confused the two experimental interpretations of relative intensity, i.e., ratio of maximum ordinates and ratio of areas. This was, at first, not thought of as a serious confusion since it was not known then that x-ray lines have such widely differing shapes, particularly widths. Of course, if the two x-ray lines in question had identical widths (preferably zero widths) and shapes the two relative intensity interpretations would be the same. But they seldom do: The observed widths of the present L series lines for Ag (47) differ from each other by as much as a factor of 7 (e.g., the β_1 to l lines). Ideally, then, an instrument of practically infinite resolving power is to be preferred. The two crystal spectrometer comes closest to meeting this requirement, but does not quite reach it. To say that the width of the spectral window is but 1/5 or 1/10 or 1/20 of the width of the x-ray line is to tell but part of the story; the indefinite extent of the window as it tails out on either side and its entire integrated effect in the observed contours is the complete story.[21] Even with the two-crystal instrument, unless operated with special crystals, such as with quartz, or with crystals in higher orders of reflection, a correction for lack of infinite resolving power must be made.

There are, therefore, two uncertainties in relative intensity determinations due to resolution, (1) inherent in the analyzing spectrometer in not meeting the requirements for either of the two experimental interpretations of relative intensity of lines of different widths and shapes, and (2) a consequence of an arbitrary resolution of overlapping structure into the proper component lines even though recorded with an instrument having infinite resolving power. These effects of resolution are in part responsible for the discrepancies in the relative intensity values that have appeared in the literature, and in particular for the differences between the present measurements and the hertofore best measurements for the silver L series lines, e.g., those of Jönsson, of Pearsall, and of Hirsh.[22]

In Table III are listed the experimental relative intensities of the AgL series lines. In the third column are the ratios of observed peaks (maximum ordinates) corrected only for the continuous and scattered background. In the fourth column are ratios of the peaks of the previous column corrected for overlapping. In the fifth column are ratios of the areas corrected for background, for overlapping, for lack of finite resolving power, for coefficient of reflection of the crystals,[23] and for absorption in the two

---

[21] The problem of the effect of the crystal diffraction patterns is carefully discussed in connection with the short wave-length limit of the continuous spectrum by DuMond and Bollman, Phys. Rev. **51**, 400 (1937) and mentioned by Kirkpatrick and Ross, Phys. Rev. **51**, 529L (1937). See also Compton and Allison, reference 20, pp. 710–722, and reference 5.

[22] A. Jönsson, Zeits. f. Physik **46**, 383 (1928), A. W. Pearsall, Phys. Rev. **46**, 694 (1934), F. R. Hirsh, Phys. Rev. **48**, 722 (1935), and Hirsh and Richtmyer, Phys. Rev. **44**, 955 (1933).

[23] The coefficient of reflection of a crystal is defined as the area contained under the diffraction pattern of the crystal on which is incident unit intensity of radiation of the wave-length contained in the pattern. In obtaining relative intensity, the correction for the variation of the coefficient of reflection is, for each crystal, the reciprocal of the ratio of the two pattern areas for the two wave-lengths in question. This correction tacitly includes the *width* of the pattern (area$\sim$(width$\times$height)) and therefore includes a correction for the resolving power. But note that this aspect of the resolving power is merely that the *intensity* which a crystal reflects is approximately inversely proportional to

windows (Cellophane, combined thickness of 0.0017 inch). The x-rays are completely absorbed in the ion chamber. The corrections for the ionization probabilities and for absorption in the target have not been made because of the difficulties in their execution at this time.

The two corrections for resolution, somewhat arbitrary as shown above, are believed to in-

---

the width of the spectral window; it says nothing about the perturbations present in an observed contour due to the *changing slope* of the true or unperturbed contour. These perturbations, referred to in the text as inherent in the spectrometer, are really characteristic of the *interactions* of the spectrometer with the spectral region under observation: The observed curve is the integral of the product of the diffraction pattern and the true contour being studied. In a sense, then, two separate corrections must be made for the lack of infinite resolving power (in addition to the arbitrary resolution of lines if they overlap). In this connection it may be mentioned that to relative intensity measurements made with a single crystal spectrometer or spectrograph should be applied, in addition to the correction for coefficient of reflection of the crystal, a correction for the change in area of the spectral window when this area is determined by slit-geometry. This correction, a resolving power correction (where the resolving power is proportional to the tangent of the Bragg angle), is the ratio of the energy extents of the spectral windows for each of the two wave-lengths. For lines of large wave-length separation this correction is significant.

TABLE III. *Relative intensities of the lines of the L series spectrum of silver ($Z=47$). The most intense line, α_1, is taken as 100. The relative areas in column 5 include corrections for background, for overlapping of neighboring lines, for lack of infinite resolving power of the spectrometer, for coefficients of reflection of the two crystals, and for absorption in the x-ray path with the exception of the absorption in the target itself.*

		PRESENT MEASUREMENTS			PREVIOUS MEASUREMENTS		
LINE	TRANSITION	OBSERVED PEAKS FROM CONTOUR	OBSERVED PEAKS (CORRECTED FOR OVERLAPPING)	AREAS CORRECTED (NOT CORRECTED FOR ABSORPTION IN TARGET)	NOT CORRECTED	CORRECTED FOR TARGET ABSORPTION, ETC.	OBSERVERS*
β_4	$L_I M_{II}$	2.34	2.1	3.9	4.6	5.8	J
β_3	M_{III}	3.7	3.6	7.2	7.4	9.4	J
β_{10}	M_{IV}	—	0.030	0.043			
β_9	M_V	0.08	0.056	0.074			
γ_2	N_{II}	—	0.36	0.66			
γ_3	N_{III}	—	0.62	1.04			
$\gamma_{2,3}'$	Satellite	—	0.013	0.029			
$\gamma_{2,3}''$	"	—	0.013	0.029			
η	$L_{II} M_I$	0.27	0.27	2.0	2.0	2.2	J
β_1	M_{IV}	58.1	58.1	49.1	53	59	J
β_1'	Satellite	—	0.6	0.84			
β_1''	"	—	0.6	0.84			
β_1'''	"	—	0.2	0.28			
β_1^{iv}	"	—	0.07	0.10			
γ_5	N_I	0.16	0.13	0.28			
γ_1	N_{IV}	5.2	5.2	4.36	9.5	12	J
γ_1'	Satellite	0.12	0.10	0.10			
γ_1''	"	—	0.026	0.026			
γ_1'''	"	—	0.019	0.036			
l	$L_{III} M_I$	0.40	0.40	4.4	4.1	4.1	J
α_2	M_{IV}	15.6	9.2	8.61	12	12	J
α_1	M_V	100	100	100	100	100	
α_3	Satellite	7.57	1.37	1.64			
α_4	"	7.14	3.9	5.0	16% of α_1		
α_5	"	—	2.13	3.0			H
α_6	"	—	1.06	1.58	33% of α_1		
α_7	"	—	0.3	0.45			H and R
β_6	N_I	0.65	0.22	0.56			
β_2	N_V	12.1	12.1	11.9	20.2	21	J
$\beta_2^{(a)}$	Satellite	—	—	—			
β_2'	"	0.694	0.586	0.50			
β_2''	"	0.64	0.49	0.63			
β_2'''	"	0.48	0.22	0.27			P
β_2^{iv}	"	—	0.14	0.22	52.2% of β_2		
β_2^{v}	"	—	0.10	0.11			
β_2^{vi}	"	—	0.04	0.05			

* J = Jönsson, 1928. Recorded at 10 kv.
H = Hirsh, 1935. Recorded at 20 kv.
H and R = Hirsh and Richtmyer, 1933. Recorded at 20 kv.
P = Pearsall, 1934. Recorded at about 17 kv.

troduce the largest uncertainty, from 2 or 3 percent in most favorable cases and perhaps as much as 700 percent in the cases of the weak satellites, such as β_2'''.

The coefficients of reflection of the crystals had been carefully determined previously.[5] As defined in terms of the second reflection in a two-crystal spectrometer, the coefficient of reflection refers to a partially polarized x-ray beam. According to the theory of crystalline reflection, an unpolarized beam is, upon reflection at 45° ($\lambda=4.28$A with calcite), completely polarized; its intensity is therefore reduced to one-half for this reason alone. With a Bragg angle different from 45° the second reflection increases the polarization by further reducing the relative intensity of the π-component, but the fractional reduction of intensity of the whole beam at the second crystal is much less than at the first crystal. The intensities (calculated, not observed) of the π- and σ-components as reflected from the first and second crystals are given as integrals of $F(l)$ and $\Phi(k)$ functions in an earlier paper.[24] From these integrals and from the definition and units of R, the coefficient of reflection, one may ascertain the approximate correction to the intensity reflected from each crystal for the variation of R with wave-length. The resultant correction for both crystals together, as a reciprocal multiplying factor for each line, is

$$R=R_A\cdot R_B=\delta^2\sec^2\theta_0\csc^2\theta_0 \times\left\{\int_{-\infty}^{\infty}\Phi_\sigma(k)dk+\int_{-\infty}^{\infty}\Phi_\pi(k)dk\right\}D^2E^2, \quad (2)$$

where D is the dispersion factor (reciprocal radians to reciprocal spectral energy units) and E is the ratio of the experimental values of R_B to the calculated values ($E\approx0.92$). The quantity δ is the unit decrement of the refractive index and θ_0 is the corrected Bragg angle. The $\Phi(k)$ functions include absorption of the x-rays in the crystals.

Until the target absorption and ionization probability corrections have been made the present relative intensity values must be considered as characteristic of the angle between the electron beam and the target face, 60°, the angle of the x-ray beam and target face, 30°, and of the tube voltage, 15 kv. These target and voltage corrections are small for lines whose wave-length separation is small and the present values may, for such lines, be taken as the approximate transition probabilities.

Argon gas at various pressures was used in the ion chamber for most of these studies. Argon is not entirely satisfactory because the K absorption edge occurs at about 3.857A, in the middle of the present wave-length range. To avoid uncertainties in the ion chamber corrections because of this absorption differential and to insure linearity of the intensity recording system for wave-lengths on either side of this absorption edge, a careful calibration was made with air at 2 atmospheres pressure and again with methyl bromide. For accurate studies of certain regions of the entire spectrum, e.g., the β_2 satellites or the $\gamma_{2,3}$ lines, and for accurate wave-length positions or for line widths and shapes, argon was used at a pressure reduced to a minimum as mentioned above; but, for the β_4 line (see Fig. 2) and for the relative intensities of the entire series, the peak intensities of the several "key" lines were taken quickly and consecutively without changing operation of the x-ray tube or the pressure of air (or of methyl bromide) in the ion chamber.

Only qualitative agreement is found between the present relative intensities and those of previous observations, Table III. Air in a point Geiger counter was used by Jönsson to detect the intensity. The photographic method was used in the other cases where comparison can be made, namely, in the measurements of the integrated satellite intensity (integrated over the total structure) by Hirsh, by Hirsh and Richtmyer, and by Mrs. Pearsall.[22]

WIDTHS

Emission lines

The observed full widths at half-maximum intensity of the Ag L series lines are tabulated in Table IV, column four. The widths corrected for the finite resolving power are listed in column five. For strong and nonoverlapping lines the

---

[24] L. G. Parratt, Phys. Rev. **41**, 561 (1932), Table III. See Compton and Allison, reference 20, p. 725, for simplification of $\Phi(k)$.

uncertainties in the observed widths are about 2 percent; in the corrected widths about 8 (guess) percent. For weak lines appearing in an overlapping multiplet structure the uncertainties may be as large as 100 percent. In the last column are given the corrected widths in electron volts.

The wide variations in the observed line widths, from 3.0 x.u. to 21.5 x.u., is very striking. Similar variations, although somewhat smaller, have been observed before in L series lines, for example, for U(92),[25] for Au(79)[2] and for Pb(82).[26] Jönsson[22] also detected variations in the widths of L series lines; he observed the AgLl line to be 3 times as wide as Ag$L\beta_1$.

No general statements about the shapes of these lines can be made except that, with rare exceptions, the lines are not symmetrical. The asymmetries are given as indices[27] in the third column of Table IV. Note that the steep side, except for the α_1 line, is the long wave-length side of the line instead of the short wave-length side as in the case of asymmetrical $K\alpha_{1,\,2}$ lines.[28]

Widths of energy levels

The widths of x-ray lines are related in some manner to the widths of the energy levels of the radiating atoms. Of the several factors contributing to the mean lifetimes of the excited

TABLE IV. *Widths of silver L series lines.*

LINE	TRANSITION	INDEX TO ASYMMETRY	OBSERVED WIDTHS (CORRECTED FOR OVERLAPPING) (SECONDS OF ARC)	WIDTHS (CORRECTED FOR RESOLVING POWER AND FOR OVERLAPPING) (X.U.)	ENERGY WIDTHS (CORRECTED) (ELECTRON VOLTS)
β_4	L_IM_{II}	0.9	330	7.1	5.9
β_3	M_{III}	1.0	360	7.8	6.6
β_{10}	M_{IV}	—	275	6.3	6.0
β_9	M_V	—	265	5.9	5.6
γ_2	N_{II}	—	400	9.7	11.0
γ_3	N_{III}	—	375	9.0	10.2
$\gamma_{2,3}'$	Satellite	—	?	?	?
$\gamma_{2,3}''$	"	—	?	?	?
η	$L_{II}M_I$	0.9	850	16.9	10.8
β_1	M_{IV}	1.0	155	3.0	2.4
β_1'	Satellite	—	225	5.0	4.0
β_1''	"	—	225	5.0	4.0
β_1'''	"	—	225	5.0	4.0
β_1^{iv}	"	—	225	5.0	4.0
γ_5	N_I	—	410	9.2	8.8
γ_1	N_{IV}	0.8	180	3.9	3.95
γ_1'	Satellite	—	200	4.5	4.5
γ_1''	"	—	200	4.7	4.7
γ_1'''	"	—	300	7.0	7.0
l	$L_{III}M_I$	0.9	1200	21.5	10.7
α_2	M_{IV}	—	162	3.1	2.2
α_1	M_V	1.05	178	3.26	2.34
α_3	Satellite	—	185	3.8	2.8
α_4	"	—	205	4.1	3.0
α_5	"	—	220	4.6	3.3
α_6	"	—	230	4.9	3.5
α_7	"	—	230	4.9	3.5
β_6	N_I	—	455	9.9	8.6
β_2	N_V	0.9	195	4.11	3.72
β_2'	Satellite	—	160	3.5	3.2
β_2''	"	—	235	5.2	4.8
β_2'''	"	—	235	5.2	4.8
β_2^{iv}	"	—	275	6.4	5.9
β_2^{v}	"	—	200	4.7	4.3
β_2^{vi}	"	—	225	5.2	4.8

---

[25] J. H. Williams, Phys. Rev. **37**, 1431 (1931).

[26] R. E. Shrader, Phys. Rev. **49**, 644*A* (1936).

[27] The index of asymmetry is defined as the ratio of that part of the line width on the long wave-length side of the maximum ordinate to that part of the width on the short wave-length side.

[28] L. G. Parratt, Phys. Rev. **50**, 1 (1936), and J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).

states involved in the emission of the line, the dominating factors have an energy distribution given by the dispersion equation,

$$I(\nu)d\nu=\frac{\Gamma}{2\pi}\frac{d\nu}{(\nu_0-\nu)^2+(\Gamma/2)^2}, \qquad (3)$$

where Γ is the full width at half-maximum intensity of these factors.[2] An x-ray line emitted by a transition between two energy states, each of whose energy distribution is of the form given by Eq. (3), has a spectral distribution of the same form when Γ is interpreted[2] as the sum of the widths of the two involved states, A and B.

$$\Gamma_{\text{line}}=\Gamma_{A\text{ state}}+\Gamma_{B\text{ state}}. \qquad (4)$$

The simple sum relation of Eq. (4) is a well-known characteristic of the product of two dispersion curves. Γ_A or Γ_B is to be interpreted as a statistical width rather than as the actual width of the energy level or state of any *one* atom. Reciprocity between mean lifetimes of energy states and widths of energy states follows from the uncertainty principle.

With this interpretation of line widths it is apparent that the widths of energy states are of considerable significance: A schematic diagram of widths of energy states, once obtained, may be used to predict widths of emission lines[29] in much the same manner as energy level diagrams are used to predict wave-lengths of lines; and observed widths may be used to check the theory.[29]

There are 15 diagram lines and 13 energy levels; but unfortunately we cannot solve for the 13 unknowns by the method of a simultaneous solution using Eq. (4) because the equations are not independent.

A solution was proposed by Richtmyer, Barnes and Ramberg,[2] which involves an independent determination of one of the energy levels from a measurement of the width of an absorption limit. With the purpose of such a solution in mind the contours of the three AgL absorption limits were recorded. In Fig. 5 is reproduced the contour of the L_{III} absorption region. The amount of "secondary" and "fine" structure[30, 31] is seen to be very large, sufficient indeed to defeat the purpose intended in recording the contour.

Parenthetically, it is interesting to note that this absorption limit contour, Fig. 5, includes, superimposed on the L_{III} absorption state, a series of resonance absorption lines. These absorption lines involve the atomic or optical energy levels for lines lying close to the main absorption edge, and involve the crystal lattice energy levels for the lines farther removed from the main edge. It seems possible that in the near future we shall obtain considerable *precise* information about the outer energy levels or zones in the nongaseous states by the analysis of such accurately recorded curves.[32]

By Eq. (4), the width of the L_{III} state is less than the width of the $L\alpha_1$ emission line by an amount equal to the width of M_V. The corrected

---

[29] This assumes that we may neglect those width factors whose energy distributions are not of the form of Eq. (3). Such factors, mentioned in an earlier paper (Phys. Rev. **50**, 1 (1936)) on $K\alpha_{1,\,2}$ lines of elements of lower atomic numbers, are probably present in most if not all x-ray lines and the relative importance of their contributions is probably greater when the shapes of the observed lines are not symmetrical or are not given by Eq. (3). Strictly speaking, this assumption is not justified in the present study and the energy level widths obtained therefrom can have only a qualitative meaning but are certainly of the correct order of magnitude.

[30] Structure within the energy region defined by the minimum ionization potential of the atom (rather, of atom $(Z+1)$) is "fine" structure (Kossel); outside of this energy region is "secondary" structure (Lindsay-Kronig). The minimum ionization potential of Cd(48) is 9 electron volts. Kossel structure is supposed to be characteristic of vapor absorbers; Kronig structure of crystalline absorbers. The type of structure in Fig. 5 close to the L_{III} edge for crystalline silver is both fine and secondary structure and the distinction is of little or no significance.

[31] It is not possible to match this structure with that calculated from Kronig's equation

$$E(n)=((n^2h^2)/8md^2), \quad n^2=\alpha^2+\beta^2+\gamma^2 \qquad (5)$$

(where α, β, γ are Miller indices, d the grating space, m the electronic mass and h Planck's constant) but agreement is not to be expected when one considers (1) that Eq. (5) does not hold for small values of n because in this energy region the electron is not "free"; (2) that we do not know just where on the contour we should take $n=0$; and (3) that we are dealing with the region of the crystal lattice containing an ion (inner, L_{III}, electron missing), the perturbations due to which are not included in the simple theory.

[32] For further treatment of these matters the reader is referred to R. Smoluchowski, Phys. Rev. **50**, 201 (1936); Mott and Jones, *Properties of Metals and Alloys* (Oxford University Press, 1936), pp. 128–131, and references; and, for a systematic study (photographic method) of the L absorption limits of elements neighboring to Ag(47), to Arne Sandstrom, "An Investigation into X-Ray Absorption Spectra," Inaugural Dissertation, Upsala, 1935. See also R. Landshoff, Rev. Sci. Inst. **9**, 143 (1938).

width of the $L\alpha_1$ line is indicated by the length of the arrow near the center of the main edge in Fig. 5. The difficulties in resolving the observed contour into the L_{III} state and the component resonance lines are at this time insurmountable. Similar difficulties are encountered in ascertaining the width of the L_I or the L_{II} state, or, as we shall see presently, of the K state from the contour of the corresponding absorption limit.

Having found no direct solution for state widths, we proceed somewhat arbitrarily to estimate the width of the L_{III} energy state as 2.0 electron volts. From this as a base the widths of all the other energy levels have been calculated. These widths are given in Table V.

A few differences are found in the trends in the widths of the energy states of silver in Table V and of the widths of the energy states of gold, Table V of Richtmyer, Barnes and Ramberg.[2] L_{II} is wider than L_{III} for silver, the reverse is found for gold. The present M_{II} and M_{III} levels are seemingly very narrow in comparison with those of gold. These and other variations between Ag(47) and Au(79) are to be ascribed apparently to variations in the Auger width. Auger widths, sensitive to variations in the electronic architecture of the atoms, have not yet been sufficiently well evaluated for further discussion.

The width of the $K\alpha_1$ line of Ag has been measured by Allison[33] as 0.28 x.u. This width, when corrected for the finite resolving power of the crystals, is about 10 electron volts. We calculate an expected width of 8 electron volts for the silver K state when we assume the width of the L_{III} state to be 2 electron volts. Ross[34] has reported 34 electron volts, uncorrected, or 25 ev, "corrected" for resolving power, for the width of the K absorption limit of silver. In conforming to the present definition of the width of an absorption limit, Ross' corrected measurement is reduced to perhaps 17 ev. The difference between 8 (calculated) and 17 (observed) is apparently to be ascribed to unresolved fine or sub-Kronig structure in the K absorption contour. The fact that irregularities in the AgL_1 contour, involving the same "optical" levels by the selection rules, are found in the present study close to the main absorption edge means that such resonance absorption structure must be present, although as yet undetected, in the K contour also.

Resonance absorption lines are, of course, much less ambiguous when the absorber is a gas, and, indeed, have been recently measured and identified for A(18).[35] Incidentally, the width of each of these resonance lines for argon,

TABLE V. *Widths of x-ray energy states of* Ag(47).

State	Quantum Numbers		Widths Observed (electron volts)	Widths Computed (electron volts)	Remarks
	n	l			
K	1	0	25	8.0	$K\alpha_1-L_{III}$ K limit by Ross $K\alpha_1$ line by Allison
L_I	2	0	10(?)	5.3	$L_{III}+\beta_9-\alpha_1$, $L_{III}+\beta_{10}-\alpha_2$
L_{II}	2	1	6(?)	2.2	$L_{III}+\eta-l$, $L_{III}+\beta_1-\alpha_2$, $L_{III}+\gamma_5-\beta_6$
L_{III}	2	1	(2.0)	2.0	Basis of interpretation ($\alpha_1=L_{III}+M_V$)
M_I	3	0	—	8.6, 8.7	$\eta-L_{II}$, $l-L_{III}$
M_{II}	3	1	—	0.6	β_4-L_I
M_{III}	3	1	—	1.3	β_3-L_I
M_{IV}	3	2	—	0.2, 0.7, 0.2	β_1-L_{II}, $\beta_{10}-L_I$, α_2-L_{III}
M_V	3	2	—	0.34	α_1-L_{III}
N_I	4	0	—	6.6, 6.6	β_6-L_{III}, γ_5-L_{II}
N_{II}	4	1	—	5.7	γ_2-L_I
N_{III}	4	1	—	4.9	γ_3-L_I
N_{IV}	4	2	—	1.8	γ_1-L_{II}
N_V	4	2	—	1.7	β_2-L_{III}

---

[33] S. K. Allison, Phys. Rev. **44**, 63 (1933).

[34] P. A. Ross, Phys. Rev. **44**, 977 (1933).

[35] Richtmyer and Parratt, Phys. Rev. **53**, 678*A* (1938).

one of which is very sharp and easily measured, gives directly the width of the K state of argon, the width of the optical level ($4P$) being negligible.

Widths of double ionization energy levels

Following a lead given in a recent paper by Richtmyer and Ramberg,[16] the width of the state, either initial or final, in the emission of a satellite (a double ionization) line may be taken as the sum of the widths of the two states (each of double ionization) involved. We may tentatively use the state widths derived from widths of single ionization lines, as listed in Table V. This is done with the argument that ". . . the absence of a single other electron is not likely to influence materially the probability per unit time that either one of the vacancies will be filled."[16]

As an example, the $L\alpha$ satellites arise from transitions $L_{III}M_{IV,V}$ to $M_{IV,V}M_{IV,V}$, so we may expect the widths of the $L\alpha$ satellite lines for silver to be $2+0.3+0.3+0.3=2.9$ electron volts. Actually, the observed widths of the $L\alpha$ satellite lines are from 2.8 to 3.5 electron volts as listed in Table IV. That the lines α_5, α_6 and α_7 are wider than 2.9 ev may be an indication that the observed contour should be resolved into more component lines than the five in the present analysis. Indeed, the calculations of Richtmyer and Ramberg[16] treat fifteen $L\alpha$ satellite components, transition ($2p3d\rightarrow 3d^2$), of which 8 are fairly intense. Only five components are drawn in the present experimental study because only five pronounced irregularities are present in the observed contour, but if one chose to so interpret the conclusions of the theory, one might sketch under the observed contour all fifteen lines.

The case of the widths of the satellites of $L\beta_2$ is especially interesting. These satellites supposedly arise from the transitions $L_{III}M_{IV,V}\rightarrow N_VM_{IV,V}$: the expected width for the satellites is $2+0.3+1.7+0.3=4.3$ electron volts, using the values in Table V. The observed widths of the $L\beta_2$ satellites are, with the exception of the β_2' line, from 4.8 to 5.9 ev. Here again we might sketch in more components than are indicated in Fig. 4, perhaps as many as the theoretical forty,[16] thereby reducing the widths of all the components to, say, 4.3 ev.

The $L\beta_2'$ satellite line is an unruly one. Surprisingly, this line is *narrower* than its "parent" line $L\beta_2$; the doubly ionized states involved in this satellite emission are longer lived than the singly ionized states which emit $L\beta_2$. No reasonable resolution of the observed contour, Fig. 4, can avert this conclusion. Another resolution, which eliminates β_2^{vi}, and makes β_2''' less wide but asymmetrical (with an index much less than unity) may possibly force the width of β_2' to equal β_2, but the shape of β_2' is then unreasonable. It is perhaps unnecessary to point out that the addition of more components of equal or of less widths serves to *decrease* component widths rather than to increase them.

That the β_2' line is less wide than the parent line β_2 may indicate that the absence of the second electron does materially influence the probability per unit time that the N_V vacancy will be filled. The absence of the second electron may disturb the energy relations of the various electron shells a sufficient amount to materially decrease the sensitive Auger width of N_V. No calculations on this point have been made. No matter what the explanation may be for the narrow β_2' line, one may not use with impunity the sum of the observed widths of singly ionized states to obtain the width of a satellite state; rather, in any given case, one must wait for supporting theoretical calculations. Consequently, in the present status of the investigation, no component satellite line has been assumed in a complex structure on the criterion of satellite widths.

It is quite possible that, while the argument presented above may not be valid in some cases, it may hold in other cases. That the satellites of β_1 are somewhat wider than the "expected" width of 3 ev may indicate either that their background, the side of β_1, has been sketched in too low or that more than four components are really present. Two of the satellites of γ_1 are of the "expected" width but the third, γ_1''', has some 2.5 ev excess width, possibly "evidence" of additional unresolved components.

One would expect the relation to hold best with the $K\alpha$ satellite states, because the Auger widths in the $L_{II,\ III}$ states are of much less relative importance. Experimentally, the component widths of the $K\alpha_{3,\ 4}$ group of satellites vary from 1.5 to 3 times the widths of the "parent" lines for element S(16) to Pd(46),[36] but we do not yet have information about the widths of the single ionization states.

---

[36] L. G. Parratt, Phys. Rev. **50**, 1 (1936); Shaw and Parratt, Phys. Rev. **50**, 1006 (1936).

JULY 15, 1938 PHYSICAL REVIEW VOLUME 54

The Continuous Absorption Spectrum of Iodine Monochloride in the Ultraviolet

JOHN L. BINDER
Pure Oil Company, Chicago, Illinois

(Received May 27, 1938)

It is shown that the absorption of light in ICl gas follows Beer's law, at least up to the concentrations used here, namely 4×10^{-4} mole/l. The absorption coefficients of ICl were measured at a number of wave-lengths and at several temperatures in the ultraviolet continuous band and the partial absorption coefficients derived from them. The effective amplitude of vibration of the electron producing this band was determined from the absorption coefficient curves. An attempt to measure the dissociation of ICl spectral-photometrically showed that the visible continuous band and the ultraviolet continuous band broadened out at high temperature to completely overlap the continuous ultraviolet band of Cl_2.

INTRODUCTION

As part of a program on the study of the continuous absorption of the halogens, the measurement of the absorption coefficients of ICl was undertaken. The continuous band reported[1] with maximum at 2400A was chosen rather than that in the visible because the iodine absorption on the short wave side is so weak that it can be neglected and the Cl_2 absorption on the long wave side is known. Such is not the case with the visible ICl continuum.

EXPERIMENTAL

The ICl was prepared[2] by mixing atomic proportions of pure solid I_2 and pure liquid Cl_2 in a closed vessel which had been evacuated. Samples for use were withdrawn into evacuated bulbs through "Breakoffskies." The compound was analyzed by titrating weighted amounts with standard $Na_2S_2O_3$ and also by precipitating the silver halides followed by a determination of the Ag in the precipitate. The results of the analyses agreed well and were within 1 percent of the theoretical mole percent values. In subsequent calculations the atomic ratio is taken to be 1 : 1 for this sample.

Since ICl decomposes readily and is very reactive, the quartz absorption cells were filled and the concentration of the gas in them found in the following manner. A weighed bulb of ICl was broken in an evacuated 6 l flask to which the cell was connected. When equilibrium was reached the cell was sealed off and the balance of the ICl frozen into a side tube on the flask which was then sealed off. The amount of ICl in the tube was found by titrating with $Na_2S_2O_3$ and a check obtained by weighing the broken glass of the bulb.

The absorption coefficients were measured by means of photographic photometry. The same type of apparatus and disposition was used as employed by Gibson and Bayliss[3] in the measurement of the absorption coefficients of Cl_2. However, the details of spectral photographic photometry were carried out as discussed by Ornstein, Moll and Burger.[4]

The same procedure of photographing the ICl spectrum and the calibration spectra was em-

---

[1] Cordes and Sponer, Zeits. f. Physik **63**, 338 (1930).

[2] By Elizabeth P. Baxter.

[3] Gibson and Bayliss, Phys. Rev. **44**, 188 (1933).

[4] Ornstein, Moll and Burger, *Objektive Spektralphotometrie* (Vieweg u. Sohn, Braunschweig 1932).