NOVEMBER 15, 1934 PHYSICAL REVIEW VOLUME 46

The Widths of the L-Series Lines and of the Energy Levels of Au(79)

F. K. RICHTMYER,* S. W. BARNES AND E. RAMBERG, *Cornell University*

(Received September 1, 1934)

Following a résumé of the Weisskopf-Wigner theory of the shape of spectral lines, and, making certain simplifying assumptions, an expression is derived for the shape of an x-ray absorption discontinuity for the case where absorption is due to the ejection of electrons from inner orbits to the continuum of unoccupied Fermi-Sommerfeld levels. If these levels be assumed equally distributed, the curve (μ *vs.* λ) is a simple arctangent, from which the width of the associated energy level (K, $L\cdots$), corresponding to the full width of half-maximum of a radiated line, may be read directly. A more complicated expression results if the Fermi-Sommerfeld levels be not equally distributed. It is shown that the predicted shape of an absorption limit agrees reasonably well with the observed shape of the L_{III} limit of Au(79), the width of which was found to be 4.4 volts. Data are presented on the widths of some 23 lines in the L-series of Au(79), obtained by a two-crystal spectrometer. These widths, corrected for effect of the crystals, vary from 7.6 to 20.8 volts. Making use of the conclusion of Weisskopf and Wigner, that the width of a line may be interpreted as the sum of the widths of the energy states involved, and starting from the value 4.4 volts for the width of the L_{III} state, the widths of the several L, M, N and O states of Au(79) are computed. For a given total quantum number n, the width decreases with increasing orbital quantum number l. States having the same value of n, l have nearly the same width. For any given l, the L states are narrowest.

I. Introduction

THE advent of the two-crystal spectrometer has given impetus to the study of the shapes of x-ray lines; several comprehensive investigations have been recently reported. For example Williams[1] studied the widths of twelve of the L-series lines of U(92), using the Ehrenberg-Mark-Schwarzschild[2] equation

$$W_T=(W_O{}^2-W_R{}^2)^{\frac{1}{2}} \qquad (1)$$

to obtain the true full width W_T at half-maximum intensity from W_O, the observed width with the crystals in the $(1, +1)$ position, and W_R, that of the $(1, -1)$ rocking curve. It is now known that this equation is in general not applicable, since neither the $(1, -1)$ nor the $(1, +1)$ rocking curves follow the Gauss law of errors upon which the equation is based. More recently Williams[3] has reported measurements on the lines $L\alpha_1$, $L\beta_1$, $L\beta_2$ and $L\gamma_1$ for seven elements from W(74) to Bi(83), no correction being made for the finite resolving power of the crystals on account of the uncertainty of the correct relation that exists among W_T, W_O and W_R.

In a recent paper[4] on the widths of the diagram lines in the K-series of W(74) the authors have shown that for those lines and spectral regions where *true* line shapes and $(1, -1)$ rocking curves are given by the Hoyt[5] equation

$$y=a/[1+(x/b)^2] \qquad (2)$$

(a is the maximum ordinate; b, the half-width at half-maximum) one may use, to correct for the effect of the crystals, the equation

$$W_T=W_O-W_R. \qquad (3)$$

As will be seen from the present work, there is good reason to believe that, in accordance with the theory of Weisskopf and Wigner,[6] discussed below, an equation of the form of (2) represents with surprising accuracy the shape of an x-ray line. Wherever Eq. (2) applies, it and Eq. (3)—or, as will be shown below, an empirical modification of the latter—provide the tools for determining the true widths of x-ray lines from observed data.

Now, all theory aside, one might confidently expect that the width of a given spectral line would be determined by the width—or some quantity analogous thereto—of each of the energy states connected with the emission of the

---

* The senior author wishes to express his indebtedness to the Heckscher Research Council of Cornell University for a grant in aid of this research.

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

[2] W. Ehrenberg and H. Mark, Zeits. f. Physik **42**, 807 (1927); M. M. Schwarzschild, Phys. Rev. **32**, 162 (1928).

[3] J. H. Williams, Phys. Rev. **45**, 71 (1934).

[4] F. K. Richtmyer and S. W. Barnes, Phys. Rev. **46**, 252 (1934).

[5] Archer Hoyt, Phys. Rev. **40**, 477 (1932).

[6] V. Weisskopf and E. Wigner, Zeits. f. Physik **63**, 54 (1930); V. Weisskopf, Phys. Zeits. **34**, 1 (1933).

line. If so, a systematic study of the widths of as many as possible of the lines in each of the x-ray series, K, L, M . . . , for a given element should shed some light on the widths of the corresponding energy states. Accordingly, the present paper reports measurements on some twenty-three of the L-series lines and on the L_{I}, L_{II} and L_{III} absorption limits of Au(79); and also gives preliminary estimates of the widths of the several L, M . . . energy states of that element. It is hoped that similar data for the K- and the M-series lines of Au(79) will be reported from this laboratory later. As a by-product there are also reported: (1) relative intensities of the lines in each of several groups and (2) new values of the wave-lengths of several lines not heretofore completely resolved.

II. Theory of the Shapes of Lines and Absorption Limits

As Weisskopf[6] has pointed out, three factors serve to broaden out, and to determine the shape of, a spectral line. These are, in classical language, the radiation damping of the emitting atom, its heat motion, and the effects of neighboring atoms. Since the frequency width due to the first factor increases in proportion to the square of the frequency (Eq. (5)), while the effect of the remaining factors is proportional to the first or lower powers of the same, the effect of radiation damping predominates in the case of x-rays of short wave-length: Therefore the observed shape of an x-ray line, suitably corrected for the finite resolving power of the spectrometer used, is usually defined as the *true* line shape and very closely approximates the "natural line shape" of the spectral line in question.[7]

Classical theory treated the radiating atom as a damped harmonic oscillator with a displacement $A(t)$ given by

$$A(t) = A_0 e^{-\pi\Gamma t} \cos\,(2\pi\nu_0 t + \varphi). \tag{4}$$

Here A_0 is the initial amplitude of the oscillator, ν_0 its undamped frequency, and φ a phase constant. The rate at which the oscillator loses energy, and hence the damping coefficient $2\pi\Gamma$, are determined by the frequency of the oscillation:

$$\Gamma = (4\pi/3)(e^2\nu_0^2/mc^3). \tag{5}$$

For not too heavily damped vibration, that is, for $\Gamma \ll \nu_0$, the spectral distribution of the radiation from such an oscillator is:[6]

$$J(\nu)d\nu = \frac{\Gamma}{2\pi}\,\frac{d\nu}{(\nu_0-\nu)^2+(\Gamma/2)^2}, \tag{6}$$

so that on a frequency scale Γ is simply the full width at half-maximum of the line emitted. On a wave-length scale this width, corresponding to (5), becomes 0.12 X.U., independent of frequency.[8] A. H. Compton,[9] in 1922, was able to show that observed x-ray line widths were much greater than this.

The mean life τ of an atom in its excited state (represented classically by the oscillator with its initial amplitude) is, by definition,[10] equal to the reciprocal of the damping factor:

$$\tau = 1/2\pi\Gamma. \tag{7}$$

A quantum-mechanical treatment based on Dirac's radiation theory[11] led to a formula similar to Eq. (6) for the natural shape of a spectral line, but with a changed meaning for Γ. If we denote the initial state by A, the final state by B, we have according to Weisskopf and Wigner[12] for the distribution of energy

$$J_{AB}(\nu)d\nu = \frac{\Gamma_A+\Gamma_B}{2\pi}\,\frac{d\nu}{(\nu_{AB}-\nu)^2+((\Gamma_A+\Gamma_B)/2)^2}, \tag{8}$$

where

$$\nu_{AB} = \nu_A - \nu_B = (E_A - E_B)/h \tag{8a}$$

and

$$\left.\begin{aligned} \Gamma_A &= 1/2\pi\tau_A = \sum_{E_C \leq E_A}{}'(C)\gamma_{AC}; \\ \Gamma_B &= 1/2\pi\tau_B = \sum_{E_D \leq E_B}{}'(D)\gamma_{BD}. \end{aligned}\right\} \tag{8b}$$

---

[7] "Natural," because it is an intrinsic property of the atom, unaffected by its momentary motion or position relative to other atoms. It must be mentioned, on the other hand, that, due to the close linkage, the effect of neighboring atoms in solids is not altogether negligible, as has been shown by the work of L. G. Parratt, Phys. Rev. **45**, 364 (1934) on the widths of x-ray lines from alloys.

[8] G. E. M. Jauncey, Phys. Rev. **19**, 64 (1922).

[9] A. H. Compton, Phys. Rev. **19**, 68 (1922).

[10] "Mean life" is here defined as the time in which the square of the amplitude is reduced to a fraction $1/e$ (e = Napierian base) of its initial value.

[11] V. Weisskopf and E. Wigner, Zeits. f. Physik **63**, 54 (1930); see also L. Landau, Zeits. f. Physik **45**, 430 (1927). J. C. Slater, Phys. Rev. **25**, 395 (1925), obtained similar formulas on the basis of a modification of the old quantum theory.

[12] Excluding the possibility of the successive emission of two quanta of equal frequency by the same atom.

Here ν_{AB}, the frequency corresponding to the center of gravity of the line, is equal to the difference in the term values ν_A and ν_B of the initial and the final state, and this in turn is equal to the difference of the atomic energies E_A and E_B of the same states divided by Planck's constant, h; $2\pi\gamma_{AC}$ is the probability that, in unit time, a transition takes place spontaneously from state A to any other state C, necessarily of lower or equal[13] energy. The sum of the quantities $2\pi\gamma_{AC}$ for all such states C is hence the probability that, in unit time, an atom originally in state A leaves this state changing over to any other. If there are altogether N atoms in state A the most probable decrease in this number in time dt becomes, by (8b): $dN=-2\pi\Gamma_A N dt$, which, integrated, leads to the relation $N=N_0 e^{-2\pi\Gamma_A t}$, N_0 being the number of atoms in state A at $t=0$. $2\pi\Gamma_A$ is thus the reciprocal mean life of the state A and, similarly, $2\pi\Gamma_B$ the reciprocal mean life of the state B.

According to Eq. (8) the width of any line depends on the life of both the initial and the final state of the emitting atom. If, making use of a picture given in an early paper by Schrödinger,[14] we were to regard the emission of radiation as associated with "beats" between the characteristic oscillations of the atom in the initial and final state, the time-decay of *each* of these states would contribute to the "fading," and hence to the spectral breadth, of the wave train emitted.

The form of the frequency distribution given in Eq. (8) immediately suggests as an alternative point of view the concept of unsharp levels with exact fulfillment of Bohr's frequency condition in every emission or absorption process.[15] Thus if the initial state A has the width Γ_A and frequency distribution

$$J_A(\nu)d\nu=\frac{\Gamma_A}{2\pi}\frac{d\nu}{(\nu_A-\nu)^2+(\Gamma_A/2)^2} \tag{9}$$

and analogously for the final state B, the frequency distribution for the transition $A\to B$ will be

$$J_{AB}(\nu)d\nu=\int_{\nu'=0}^{\infty} J_A(\nu')J_B(\nu'-\nu)d\nu' d\nu, \tag{10}$$

which, on performing the integration, yields Eq. (8). *The width of the line is thus equal to the sum of the widths of the initial and the final state.* That is

$$W_T=\Gamma_A+\Gamma_B, \tag{11}$$

where W_T is the true width of the line emitted in transition from state A to state B. Both Eq. (8) and the concept of unsharp levels lead to incorrect results if quanta of like frequency may be emitted by the atom in successive stages.

The theory of Weisskopf and Wigner applies to line shapes in absorption as well as in emission. It is therefore possible, by making a suitable series of assumptions, to predict the shape of an absorption limit as *experimentally measured*. Let us, for example, consider an atom in which an electron has been transferred from a specified inner shell to the exterior. Subject to the selection rules for the excitation process, the resulting system may occupy any one of a close sequence (or continuum) of states E of energy greater than, or equal to, E_0, the state in which the ejected electron is in the lowest level (virtual orbit or conduction level) which is normally unoccupied. If we apply the theory of Weisskopf and Wigner to the problem of the absorption of radiation by atoms in the normal state (A), restricting our attention to processes involving the removal of an electron from the specified inner shell, we find for the corresponding partial absorption coefficient $K(\nu)$ in the neighborhood of the absorption limit:[16]

$$K(\nu)=C\sum_{\nu_{EA}=\nu_{E_0A}}^{\nu_{EA}=\infty}(E)\gamma_{EA}\left(\frac{\Gamma_E/2\pi}{(\nu_{EA}-\nu)^2+(\Gamma_E/2)^2}\right). \tag{12}$$

Here C is a constant. $2\pi\Gamma_A$, the reciprocal life of the normal state in the presence of the radiation, is extremely small compared to $2\pi\Gamma_E$, that of the excited state, and has been neglected in comparison with the latter in setting up the formula. Furthermore $2\pi\Gamma_{EA}$, the transition probability from state E to the normal state, is for a given

---

[13] Thus including the probabilities of radiation-less transitions (Auger jumps) in our consideration; see G. Wentzel, Handbuch der Physik **24**, Part 1, 768 (1933).

[14] E. Schrödinger, Ann. d. Physik **79**, 361 (1926).

[15] See, e.g., R. Becker, Zeits. f. Physik **27**, 173 (1924).

[16] A discussion of the derivation and the assumptions underlying this formula is to be found in the appendix.

sequence of energy levels[17] practically constant for intervals large compared with the width of the excited states.[18] Finally, Γ_E can be taken to be the same for all states E, since the most probable processes that reduce the life of the given excited state E are such as involve the filling of the vacancy in the specified inner shell by electrons from shells nearest to it; and these processes are practically independent of the condition of the ejected electron. For example, if the specified inner shell is the L_{III} shell of a heavy atom, we are justified in calling the corresponding Γ_E simply the width of the "L_{III} state" (i.e., the state of an atom lacking one L_{III} electron). This width Γ_E is at the same time the full width at half-maximum of the line which would be emitted if the atoms which have been excited to state E would return directly to the normal state.

We thus see that the form of the absorption curve in the neighborhood of a limit depends on (1), Eqs. (8) and (2) the distribution of free levels at the periphery of the internally ionized atom (the states beyond the "Fermi limit" of occupied states in the case of a metal). If now, in the absence of adequate information on this point, we make the simplest assumption possible, that is, that the distribution of these peripheral levels is uniform on an energy scale, we can replace the summation over the states E in Eq. (12) by an integration with respect to their term values. Replacing γ_{EA} by a constant[19] and recalling that $\nu_{EA}=\nu_E-\nu_A$ we find for the partial absorption coefficient $K(\nu)$:

$$K(\nu)=C'\int_{\nu_{E_0A}}^{\infty}\frac{(\Gamma_E/2\pi)d\nu_{EA}}{(\nu_{EA}-\nu)^2+(\Gamma_E/2)^2}$$

$$=C'\left\{\frac{1}{2}-\frac{1}{\pi}\arctan\left(\frac{\nu_{E_0A}-\nu}{\Gamma_E/2}\right)\right\}. \qquad (13)$$

Here C' is a new constant.

The general principles involved in the derivation of Eq. (13) may be made clearer by Fig. 1 in which we have represented the absorption coefficient $K(\nu)$, as given by Eq. (13), as a function of the frequency ν of the absorbed radiation, on the assumption that the excited levels E of the atom have a width $\Gamma_E=5$ electron volts and form an evenly spaced, close, sequence from E_0 toward higher energies. The curve $ABCDE$ (solid line) for the absorption coefficient results from the superposition of the evenly spaced, identical absorption lines corresponding to the several atomic states E. The horizontal separation of the two points B and D, where the curve reaches $\frac{1}{4}$ and $\frac{3}{4}$, respectively, of its asymptotic ordinate C' for high frequencies, is defined as the width of the limit, which is seen to be identical with the full width at half-maximum, Γ_E, of any one of the absorption lines, *in exact correspondence to the full width at half-maximum of a radiated line.*[20] The even distribution of energy levels is represented below the curve by the horizontal line GH which is cut off sharply on the low frequency side at $\nu_E=\nu_{E_0}$.

If, on the other hand, considering the absorption by a metal, we suppose the distribution of levels E to correspond to that of a Fermi gas of free electrons,[21] we must multiply the integrand in Eq. (13) by a weight factor $g(\nu_E)$:

$$g(\nu_E)=\text{const.}\cdot(\nu_i+\nu_E-\nu_{E_0})^{\frac{1}{2}},$$

since the density of the levels on a frequency scale increases with the square root of the (kinetic) energy of the electrons. Here, ν_i measures the difference between the mean potential energy of an electron within the crystal lattice and the total energy of an electron occupying a state corresponding to the Fermi limit. In the case of gold the value of ν_i corresponds to about 10 electron volts.[22] Carrying out the integration

---

[17] That is, a succession of energy levels having the same angular quantum numbers.

[18] A. Sommerfeld and H. Bethe, Handb. d. Physik **24**, Part 2, 462 (1933).

[19] This is legitimate if we restrict our considerations to the immediate neighborhood of the absorption limit, since then the integrand is appreciable for only a small range in ν_{EA} on either side of ν_{E_0A}.

[20] The method of determining the width used by P. A. Ross, Phys. Rev. **44**, 977 (1933) would give $\pi\Gamma_E/2$ for the width of the limit.

[21] A. Sommerfeld and H. Bethe, Handb. d. Physik **24**, Part 2, 336 (1933). The calculations of J. C. Slater, Phys. Rev. **45**, 794 (1934), on sodium indicate that this assumption is reasonable in the case of the alkalis and, hence, perhaps also in the case of the noble metals. However, it should be emphasized that an internally ionized atom is effectively a foreign ion in the crystal lattice, as pointed out below. We disregard fine structure effects for the moment.

[22] R. deL. Kronig, Handb. d. Physik **24**, Part 2, 302 and 320 (1933). The mean potential energy of an electron in the interior of a crystal referred to that in free space is determined by electron diffraction experiments; and the electron energy corresponding to the Fermi limit, by the

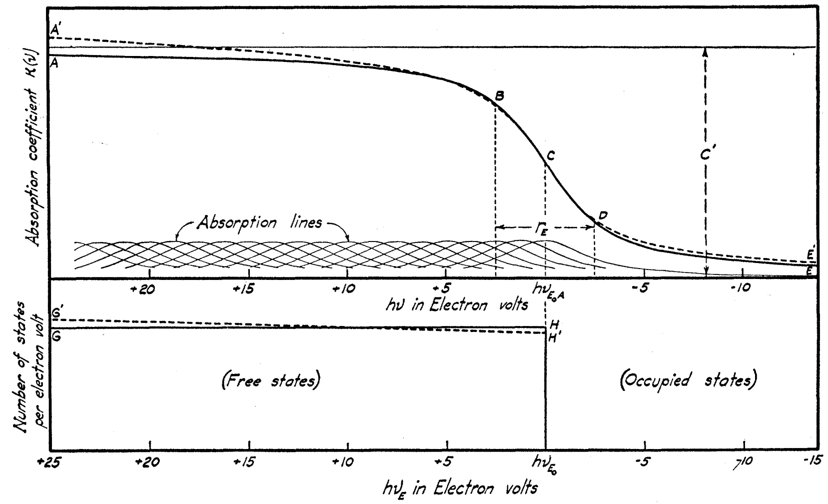


FIG. 1. Plot of Eq. (13), full line $ABCDE$ and Eq. (14), dotted line $A'CE'$. The individual absorption lines whose summation gives the predicted shape of the absorption limit, are shown below, for the case of equal distribution of levels (Eq. (13)).

for this case we obtain for $K(\nu)$

$$K(\nu)=C''\left\{A\left[\arctan\frac{B}{(2\nu_i)^{\frac{1}{2}}-A}+\arctan\frac{B}{(2\nu_i)^{\frac{1}{2}}+A}\right]+\frac{1}{2}B\log_e\left(\frac{\nu_i+D+(2\nu_i)^{\frac{1}{2}}A}{\nu_i+D-(2\nu_i)^{\frac{1}{2}}A}\right)\right\}, \quad (14)$$

where

$$\begin{aligned}A&=(D+[\nu_i+\nu-\nu_{E_0A}])^{\frac{1}{2}},\\ B&=(D-[\nu_i+\nu-\nu_{E_0A}])^{\frac{1}{2}},\\ D&=([\nu_i+\nu-\nu_{E_0A}]^2+[\Gamma_E/2]^2)^{\frac{1}{2}},\\ O&\leq\arctan[B/((2\nu_i)^{\frac{1}{2}}\pm A)]\leq\pi,\\ C''&=\text{constant}.\end{aligned}$$

Eq. (14) predicts an asymmetrical absorption limit: it is steeper on the long wave-length side. The width corresponding to an absorption line cannot be determined as readily as from Eq. (13). In Fig. 1 the absorption coefficient $K(\nu)$, as given by Eq. (14) for $\Gamma=5$ electron volts and $\nu_i=100$ electron volts, is represented by the broken curve $A'CE'$, the constant C'' having been adjusted so as to have the same ordinate $(C'/2)$ at the center of the limit as the full curve corresponding to Eq. (13). In the case of curve $A'CE'$, corresponding to Eq. (14), the distribution of levels is not quite uniform, and is indicated by the dotted curve $G'H'$ below: the individual absorption lines, from whose superposition the absorption curve may be constructed, lie progressively closer together toward higher frequencies.

We shall discuss in Section V below the agreement between Eqs. (13) and (14) and the experimental data on absorption limits.

Approaching finally the question of the fine structure superposed on the absorption curve in the neighborhood of the limit, we have to consider primarily two effects: (1) In a crystal, the existence of forbidden energy bands for electrons moving in a given direction, to which Kronig first called attention;[23] (2) In a monatomic vapor, the existence of discrete, unoccupied levels, which Kossel has pointed out as source of fine structure of x-ray absorption limits.[24] Effects of both types may have to be considered in interpreting the structures of the absorption edges of matter in still different form, e.g., polyatomic gases.[25] The secondary structure predicted by Kronig for the absorption edge of a crystal consists in oscillations of the absorption index covering a range of some hundred volts on the short wave-length side of the edge. His method of calculating the location of the maxima and

---

threshold value for the photoelectric effect. It is reasonable to regard the Fermi limit as sharp, as its width, in the cases here considered, is of the order of 1/100 of that of the absorption limit. See Sommerfeld and Bethe, reference 18, p. 466.

[23] R. de L. Kronig, Zeits. f. Physik **70**, 317 (1931); **75**, 191 (1932).

[24] W. Kossel, Zeits. f. Physik **1**, 119 (1920).

[25] J. D. Hanawalt, Phys. Rev. **37**, 715 (1931); R. deL. Kronig, Zeits. f. Physik **75**, 468 (1932).

minima, which, in general, gives results in agreement with observation, is, unfortunately, least reliable in the immediate neighborhood of the edge. The range of the fine structure observed in the case of monatomic gases and foreseen by Kossell[24] is, on the other hand, equal at most to the ionization potential of the succeeding element in the periodic table—never more than a few volts. It is located on the short wave-length side of the main absorption edge.

Even in the case of crystalline matter we may expect a fine structure in the immediate neighborhood of the limit which is essentially of the nature of that predicted by Kossel. For an atom or ion from which an inner electron has been removed acts like a foreign ion in the crystal lattice: the internal ionization changes a gold atom into a form resembling an atom of mercury which has lost one valence electron. It may be expected that the lowest free states of this "mercury ion" will not be perturbed sufficiently by the neighboring gold atoms to be drawn out into wide bands of energy states, since they may lie some 10 electron volts[26] below the corresponding states for the gold atom; due to the increased effective nuclear charge the outer orbits of the "mercury ion" shrink sufficiently so that a number of free orbits can be accommodated in the space normally filled by the occupied orbits of the gold atom. We may thus expect a fine structure of the absorption limit of metallic gold covering a range of about 10 volts qualitatively similar to the structure of the absorption edge of gold vapor. This should, in view of the selection rules, be practically the same (in frequency measure) for the K and L_{I} edges on the one hand, and the L_{II} and L_{III} edges on the other.

It is evident from the above that a close relationship exists between the widths and shapes of x-ray lines and absorption limits; at the same time, it is clear that the determination of level widths from the shapes of absorption limits is a more difficult and less certain process than the determination of line widths.

Nevertheless, from the observed shape of an absorption discontinuity, one can, by adopting the theory outlined above, make an estimate of the approximate value of the width of the associated energy level; or at least can set upper and lower limits thereto. If, then, one can obtain a reasonably acceptable value for the width of any one of the x-ray energy levels, one can, by use of Eq. (11) and the measured values of the true widths of the several "diagram" lines of the respective x-ray series, determine the widths of the other x-ray levels. Specifically, we have made what we think to be a close estimate of the width of the L_{III} level of Au(79) from measurements on the L_{III} absorption discontinuity, and from that as a starting point with the data on line widths herein reported we have estimated the widths of the several L, M, N and O levels.

III. Apparatus and Method

The two-crystal spectrometer used has been described elsewhere.[27] During the greater part of the investigations it was fitted with our pair of ground and etched calcite crystals $3A+3B$.[27] However, as was ascertained later, the crystals were not in adjustment for highest resolution during the major part of the work. Curve A of Fig. 2 gives the width of the $(1, -1)$ rocking curves, as a function of wave-length, for the crystals as actually used. Curve B gives similar data after the crystals had been carefully adjusted for verticality. Curve C, drawn through the lower point, is the width obtained for a pair

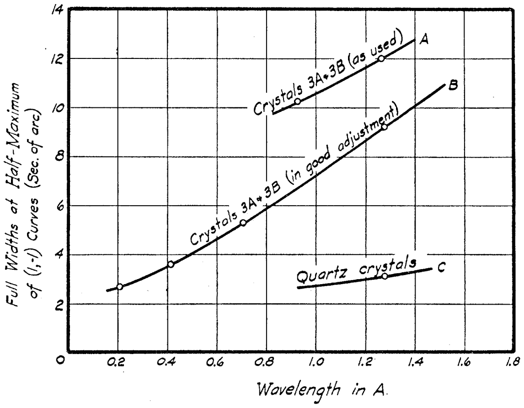


FIG. 2. Rocking-curve widths, as function of wave-length, of the crystals used, in the $(1, -1)$ position. A, for calcite crystals $3A+3B$ as used; B, for same crystals in better adjustment; C, for a quartz crystal.

---

[26] The first ionization potential of mercury (10.4 volts).

[27] F. K. Richtmyer and S. W. Barnes, Rev. Sci. Inst. 5, 351 (1934).

of ground and etched quartz crystals, $11\bar{2}0$ planes, which were kindly loaned by R. M. Bozorth and F. E. Haworth of the Bell Telephone Laboratories.

The slits limiting the vertical divergence of the x-ray beam were 1 cm high and 126 cm apart. This corresponds to an angle of maximum vertical divergence of 0.016 radian.

The ionization chamber, 3 cm in diameter and 8 cm long, is connected by a tube to a glass flask having 60 times the volume of the chamber. The chamber and flask were filled with methyl bromide to a pressure of 74 cm of mercury. There was practically no change in pressure over a period of several months.

The x-ray tube, which was fitted with a removable anode and cathode, was built with a thin glass window for transmission of the longer wave-lengths. Because mercury diffusion pumps gave trouble on account of the condensation of mercury on the gold anode,[28] the tube was evacuated by (metal) diffusion pumps using apiezon oil.

During the work on lines the tube was run at 50 kv and 20 to 25 m.a. For the study of limits it was run at 40 kv and 100 m.a.

Ionization currents were measured with a DuBridge[29] type of two tube bridge circuit, the sensitivity used being from 1000 to 10,000 mm per volt.

IV. Results

Line widths

Figs. 3(A), (B) and (C) show a "panorama" of the x-ray spectrum of Au(79) through the wave-length range comprising the L-series lines with the exception of Ll ($\lambda = 1457$ X.U.). It is important that the background due to the continuous spectrum be located with some care in order that values of half-maximum of intensity of the several lines may be accurately determined. As may be seen from the figures, a line, or particularly a partially resolved group of lines, may extend over a considerable wave-length region; so that it is necessary to go to some distance on each side of the group to locate the base line. Fortunately, the base line is nearly linear except for the discontinuities resulting from absorption in the target at the L_{I}, L_{II} and L_{III} absorption limits of gold and from the K-limit of bromine in the ionization chamber. The gold limits were located by observing the absorption in gold of x-rays from a platinum target. The wave-length of the K absorption limit of bromine was taken from Siegbahn.

It will be noted that very few of these lines, with the possible exception of $L\beta_1$, are separated far enough from other lines so that the full width at half-maximum may be read directly from the data as plotted in Figs. 3. To determine the "observed" width W_O (see Eq. (3)) of a line we must have the "observed" shape of the line apart from all other lines; that is, we must analyze Figs. 3 into the several component lines. As was pointed out by the authors,[4] if an equation of the Hoyt type, Eq. (2), gives the true shape of a line and also of the $(1, -1)$ rocking curve of the crystals used, then an equation of exactly the same form gives the shape of the line *as observed* by crystals in the $(1, +1)$ position.[30] However, as is pointed out below, in the wave-length range herein studied, the $(1, -1)$ rocking curves of the crystals depart considerably from Hoyt curves; accordingly, the *observed* line shape should not, mathematically, be Hoyt curves. Actually, however, the widths of the $(1, -1)$ curves for our calcites $3A+3B$ are only 10 or 15 percent of the widths of the lines as observed in the $(1, +1)$ position. And hence the observed shapes should not depart noticeably from Hoyt curves.

To test this conclusion observations on $L\beta_1$ were used. In Fig. 4, the observations (open circles) are compared with the Hoyt Eq. (2), the values of a and b for the latter being taken from the *observed* curve. The agreement is seen to be excellent.

---

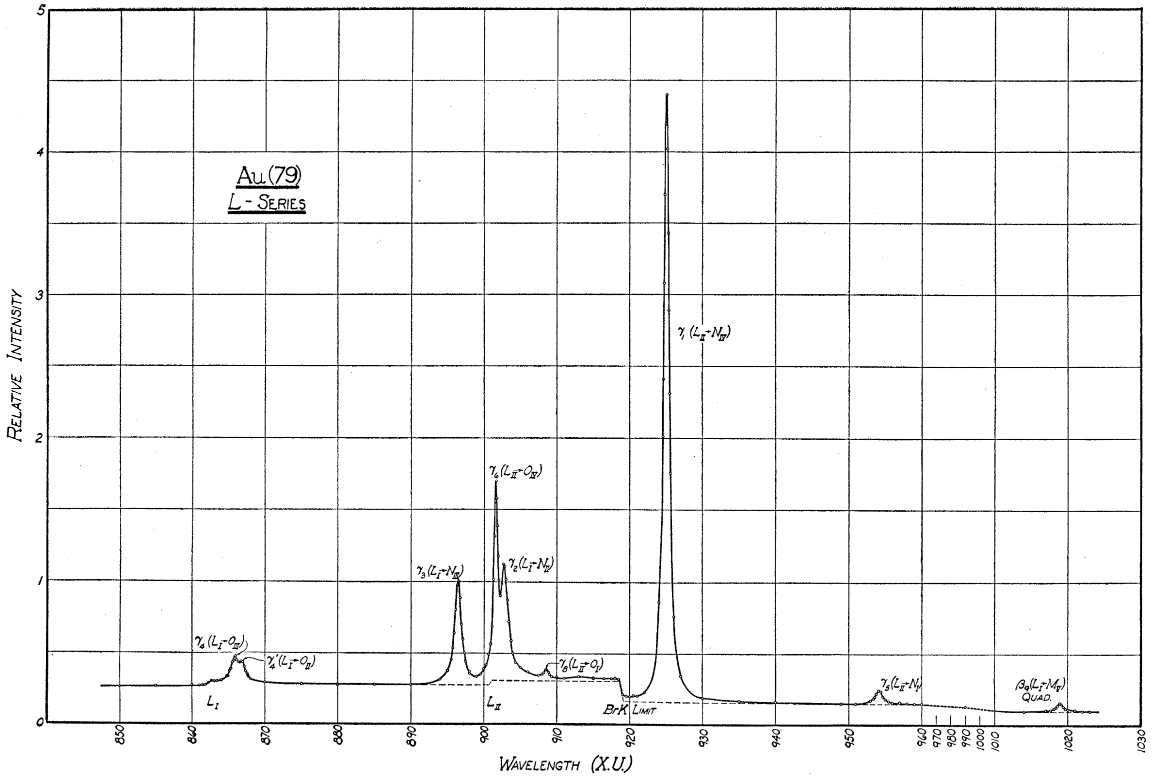
[28] In the first search for β_7 and β_7' one quite intense line was found which proved to be Hg β_1. Even after the mercury pumps had been replaced by the oil pumps and the system thoroughly cleaned some evidence of this line remained, though greatly reduced in intensity. It can be seen as the peak between Au β_7 and β_7' on Fig. 3(B).

[29] L. A. DuBridge, Phys. Rev. **37**, 392 (1931).

[30] Strictly speaking Eq. (2) represents the shape of a line plotted to a frequency scale. On a wave-length plot the equation becomes (see Richtmyer and Barnes[4])

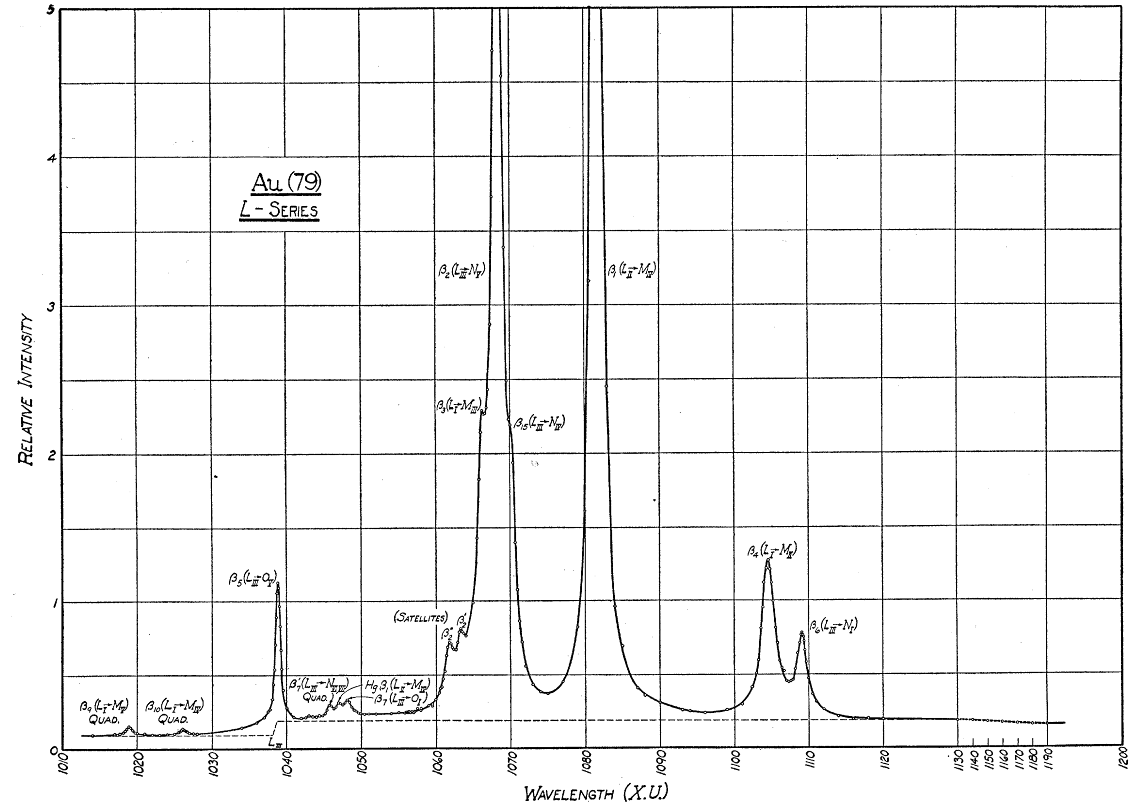
$$y_\lambda = a[1+((\lambda_0/\lambda)\cdot(x/b))^2]^{-1},$$

where λ_0 is the wave-length of the maximum ordinate. Although x-ray lines are relatively broad compared to optical lines, yet for any given line no errors greater than those of observation will be made if $(\lambda_0/\lambda)^2$ be set equal to unity.



Au (79)
L - Series
Relative Intensity
0
1
2
3
4
5
$\gamma_1 (L_{II}-N_{IV})$
$\gamma_6 (L_{II}-O_{IV})$
$\gamma_2 (L_I-N_{II})$
$\gamma_3 (L_I-N_{III})$
$\gamma_4 (L_I-O_{III})$
$\gamma_4' (L_I-O_{II})$
$\gamma_8 (L_{II}-O_I)$
$\gamma_5 (L_{II}-N_I)$
$\beta_9 (L_I-M_V)$ Quad.
L_I
L_{II}
BrK Limit
850
860
870
880
890
900
910
920
930
940
950
960
970
980
990
1000
1010
1020
1030
Wavelength (X.U.)

Fig. 3A.



Au (79)
L - Series
Relative Intensity
0
1
2
3
4
5
$\beta_2 (L_{III}-N_V)$
$\beta_1 (L_{II}-M_{IV})$
$\beta_3 (L_I-M_{III})$
$\beta_{15} (L_{III}-N_{IV})$
$\beta_5 (L_{III}-O_V)$
(Satellites)
β_2''
β_2'
$\beta_7' (L_{III}-N_{VI,VII})$ Quad.
Hg $\beta_1 (L_{II}-M_{IV})$
$\beta_7 (L_{III}-O_I)$
$\beta_9 (L_I-M_V)$ Quad.
$\beta_{10} (L_I-M_{IV})$ Quad.
L_{III}
$\beta_4 (L_I-M_{II})$
$\beta_6 (L_{III}-N_I)$
1010
1020
1030
1040
1050
1060
1070
1080
1090
1100
1110
1120
1130
1140
1150
1160
1170
1180
1190
1200
Wavelength (X.U.)

Fig. 3B.

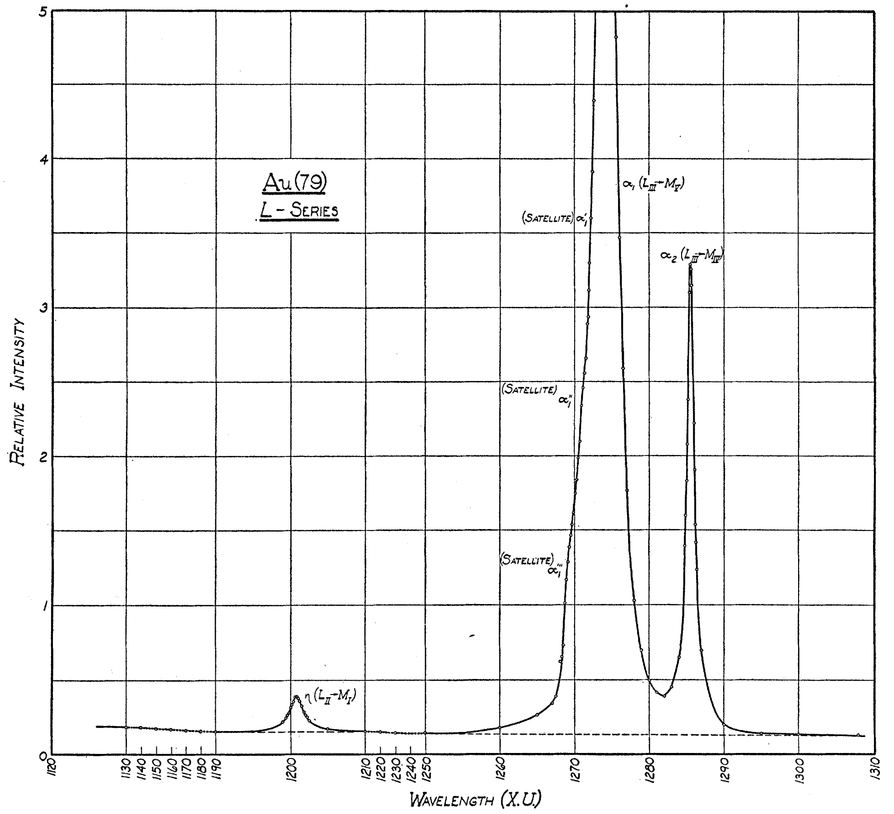


Fig. 3C.

Fig. 3. "Panorama" of the L-series of Au(79): (A), short wave-length range; (B), middle range; (C), long wave-length range. The broken horizontal line gives the continuous spectrum.

Table I. *Test of the several methods of correcting the observed width of a spectral line for the effect of the crystals.*

Gauss: $W_T=(W_O^2-W_R^2)^{\frac{1}{2}}$ Eq. (1)
Hoyt: $W_T=W_O-W_R$ Eq. (3)
Empirical: $W_T=W_O-W_R/2$ Eq. (15)

$W_R\equiv$rocking curve widths (1, −1) position
$W_O\equiv$observed line widths (1, 1) position
$W_T\equiv$true widths

Crystals: calcite except as indicated.

					W_T (X.U.) by		
Line	Observers	Crystal	W_R (sec.)	W_O (X.U.)	Eq. (1)	Eq. (3)	Eq. (15)
$L\alpha_1$	R & B	Quartz[1]	3.0″	1.08	1.078	1.035	1.058
	W	IIIA, IIIB	8.8″	1.13	1.125	1.005	1.068
	R & B	3A+3B	12.2″	1.15	1.135	0.976	1.063
$L\beta_1$	W	IIIA, IIIB	7.7″	0.785	0.779	0.675	0.730
	R & B	3A+3B[2]	7.8″	0.80	0.790	0.69	0.745
	R & B	3A+3B	11.2″	0.81	0.794	0.65	0.730
$L\gamma_1$	W	IIIA, IIIB	6.7″	0.791	0.784	0.695	0.743
	R & B	3A+3B	10.2″	0.806	0.806	0.673	0.747

W≡Williams, reference 3. R & B≡Richtmyer and Barnes.
[1] Etched Quartz crystals, 11$\bar{2}$0 planes.
[2] Carefully adjusted for minimum width.

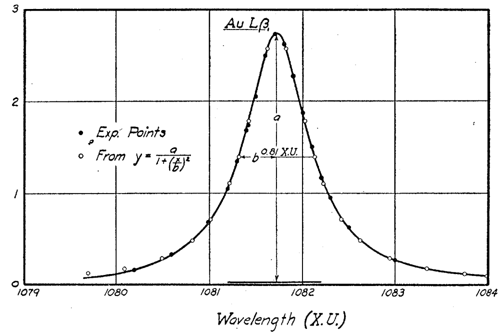


FIG. 4. The "observed" shape of Au $L\beta_1$, compared with the Hoyt equation, Eq. (2).

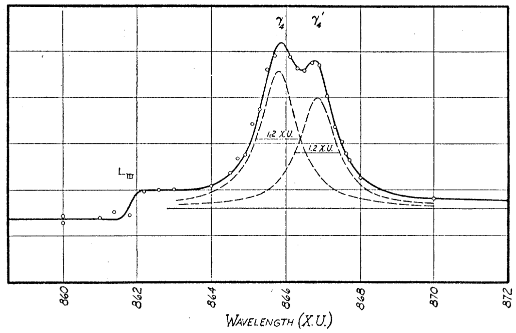


FIG. 5. Showing the method of separating the partially resolved lines γ_4 and γ_4' into the respective components, by use of Hoyt curves. The full line is the envelope of the two Hoyt curves. The circles give the observed points.

TABLE II. *The observed and the natural widths of the lines of the L-series of Au(79).*

Line	Transition	λ (X.U.)	Relative intensity	W_O (X.U.)	W_T (X.U.)	W_T (volts)
γ_4	$L_I\ O_{III}$	865.10[1]	21	1.20	1.13	18.6
γ_4'	$L_I\ O_{II}$	866.15[1]	14	1.20	1.13	18.6
γ_3	$L_I\ N_{III}$	895.81	100	1.06	0.99	15.2
γ_6	$L_{II}\ O_{IV}$	901.00	82	0.60	0.53	8.05
γ_2	$L_I\ N_{II}$	902.20[1]	100	1.20	1.13	17.2
γ_8	$L_{II}\ O_I$	907.9 [1]	3	0.70	0.63	9.5
γ_1	$L_{II}\ N_{IV}$	924.61		0.82	0.75	10.8
γ_5	$L_{II}\ N_I$	953.60		1.20	1.12	15.2
β_9	$L_I\ M_V$	1018.8	15	1.10	1.02	12.1
β_{10}	$L_I\ M_{IV}$	1026.0	8	1.20	1.12	13.1
β_5	$L_{III}\ O_{IV,V}$	1038.0	100	0.74	0.67	7.6
β_7'	$L_{III}\ N_{VI,VII}$	1045.2	9	0.95	0.87	9.8
β_7	$L_{III}\ O_I$	1047.8	15.5	1.25	1.17	13.1
$(\beta_2'+\beta_2'')$ satellites			2.5			
β_3	$L_I\ M_{III}$	1065.83[1]	16.5	2.00	1.92	20.8
β_2	$L_{III}\ N_V$	1068.01	45.5	1.04	0.96	10.3
β_{15}	$L_{III}\ N_{IV}$	1069.7 [1]	5.5	1.10	1.02	11.0
β_1	$L_{II}\ M_{IV}$	1081.28	100	0.81	0.73	7.75
β_4	$L_I\ M_{II}$	1104.22	100	2.00	1.92	19.4
β_6	$L_{III}\ N_I$	1108.63	35.5	1.70	1.62	16.3
η	$L_{II}\ M_I$	1200.3		2.35	2.27	19.3
α_1	$L_{III}\ M_V$	1273.77	100.0	1.15	1.06	8.1
α_2	$L_{III}\ M_{IV}$	1285.02	11.3	1.22	1.13	8.5
$(\alpha_1'+\alpha_1''+\alpha_1'''+\ldots)$ satellites			5.0			
l	$L_{III}\ M_I$	1456.9		3.50	3.41	19.8

[1] New values. See Table III. Remainder from Siegbahn.

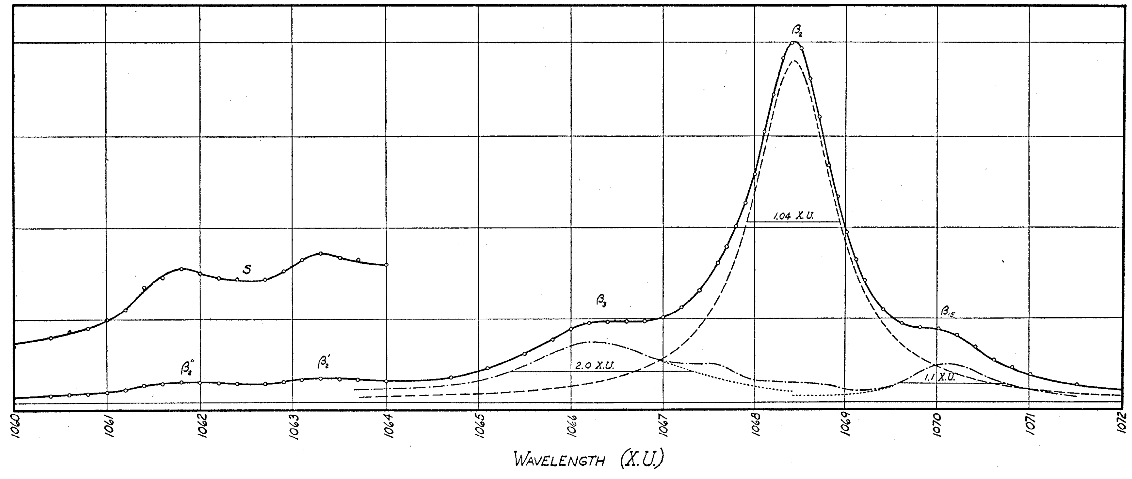


FIG. 6. The dotted lines show the Hoyt curves for the components of the group β_3, β_2 and β_{15}. (Note the residuals which have been neglected.) The satellites $L\beta_2'$ and $L\beta_2''$ are shown at the left; the line marked "S" being the satellite structure plotted to a 5× ordinate scale.

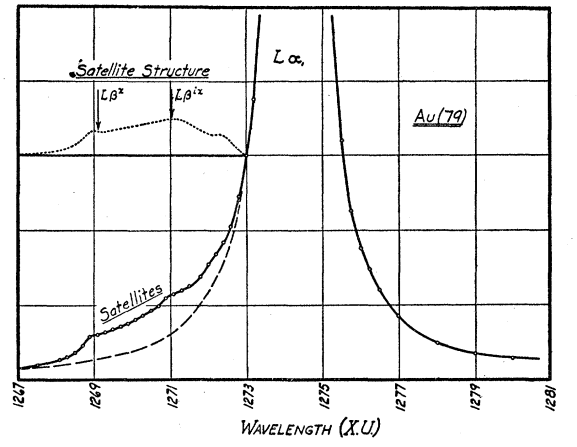


FIG. 7. The "foot" of $L\alpha_1$ of Au(79), showing the satellite structure.

Accordingly we felt justified in using Eq. (2) in analyzing Figs. 3 into the respective component lines. The method is illustrated in Figs. 5 and 6. In Fig. 5 the circles represent the observations on the close doublet γ_4, $\gamma_4'(L_{\text{I}}\rightarrow O_{\text{II, III}})$. By "trial and error" two Hoyt curves were plotted with such intensity, width and position that their envelope, the solid line, gave the best fit with the experimental points. Fig. 6 shows the way in which the group β_3, β_2, β_{15}, with the satellites accompanying β_2, was analyzed. In this case there were certain "residuals" which we neglected. The curve "S" shows the satellite structure $L\beta_2'$ and $L\beta_2''$ plotted to an open ordinate scale. Fig. 7 shows the "foot" of $L\alpha_1$, revealing the satellite structure, which is seen to consist of at least four components. Photographic methods[31] reveal only two components.

The observed widths W_O of the several lines expressed in X.U. are shown in column 5 of Table II.

Correction for the effect of the crystals

Only if the (1, -1) rocking curves of the crystals as well as the true shape of a line obey either the Gauss error curves or the Hoyt curve can Eqs. (1) or (3), respectively, be used to obtain the true width of W_T of a line from the observed widths, W_O. Fig. 8 shows that the actual rocking curve for our calcite crystals $3A$ and $3B$ at $\lambda = 0.925\text{A}$ obeys neither the Gauss error curve nor the Hoyt equation. Consequently neither Eqs. (1) or (3) can be used, the former giving too small, and the latter too large, a correction. We observe that the observations lie midway between the two theoretical curves and we were led, rather naively, to propose the correction formula

$$W_T = W_O - W_R/2. \qquad (15)$$

One obvious test of Eq. (15) is the constancy of the values of W_T which it yields for a given line which has been measured by pairs of crystals having different values of W_R. Table I shows in column 5 the widths of W_O of Au $L\alpha_1$ as observed by three different pairs of crystals, the widths of the (1, -1) rocking curves for which are given in column 4. The last three columns show the values of W_T as obtained by use of Eqs. (1), (3) and (15), respectively. The superiority of Eq. (15) is evident. This point is brought out more clearly by Fig. 9. The remainder of Table I shows similar data for $L\beta_1$ and $L\gamma_1$. The superiority of Eq. (15) is perhaps not so marked as in the case of α_1; but it does give somewhat more consistent results than Eqs. (1) and (3). Since these three lines, α_1, β_1 and γ_1, lie, respectively, near the long wave-length, the center and the short wave-length region of the wave-length range covered, we felt justified in using Eq. (15) for all the lines in the L-series.

The final values of the natural width W_T of the several lines of the L-series of Au(79), obtained by use of Eq. (15), are shown in Table II in X.U. and in volts, the values of W_R being taken from curve A of Fig. 2. The true widths vary from 7.6 volts for β_5 to 20.8 volts for β_3. The components of doublets have nearly identical widths, the long wave-length component usually being wider by an amount that is not much, if any, outside experimental error.

Wave-lengths

The careful analysis of the several groups of lines into Hoyt components, as illustrated in Figs. 5 and 6, makes possible[32] a redetermination

---

[31] F. K. Richtmyer and S. Kaufman, Phys. Rev. **44**, 605 (1933).

[32] Our spectrometer is not calibrated to give absolute values of wave-lengths with high precision. It does, however, give wave-length differences over small range of wave-lengths with great accuracy.

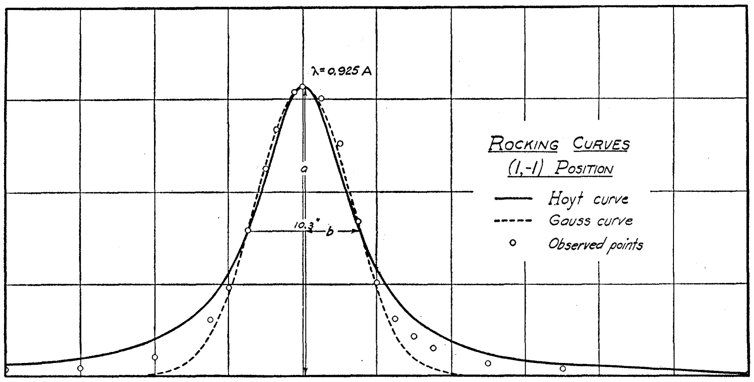


FIG. 8. The (1, −1) rocking curve of crystals $3A+3B$ at $\lambda=0.925$A showing disagreement with both the Hoyt curve and the Gauss error curve.

of the wave-lengths of the weaker components referred to Siegbahn's values for the stronger components, the "wave-length of a line" being taken to mean the wave-length of the maximum ordinate. Table III shows the new values so determined for the wave-lengths of β_3, β_{15}, γ_2, γ_8, γ_4 and γ_4'. These values are to be compared with similar data by Williams[3] for β_3 and β_{15}.

By an inspection of Fig. 3(A) it is seen that the wave-length of the center of the L_{I} absorption limit can be determined with reference to the γ_4 doublet. In the neighborhood of the L_{II} and the L_{III} edges, however, there are strong lines overlapping the edge, and it was impossible to determine the wave-length of either edge from the emission spectrum of gold. Accordingly a platinum target was substituted for the gold target and the L_{II} and L_{III} limits of Au(79) were measured by use of absorbing screens. The values so obtained (center of the limit) are included in Table III referred to Siegbahn's values of the wave-length of γ_6 and β_5, respectively. The wave-lengths of L_{I} and of γ_4 and γ_4' are determined by reference to Siegbahn's value of the wave-length of the γ_4 doublet, which value is assumed to be that of the weighted mean of the unresolved doublet.

Intensities

It has been shown by Hoyt[5] that the intensity of a line whose energy distribution is represented by Eq. (2) is $\pi a b_\nu$, where b_ν is the natural (half) width in frequency units. If line width be expressed in wave-length units, b_λ, the ratio R of the intensities of two lines of wave-length λ_1, and λ_2, respectively, is[4]

$$R=(\lambda_2/\lambda_1)^2\cdot(ab_\lambda)_1/(ab_\lambda)_2. \tag{16}$$

An accurate comparison of the relative intensities of two lines necessitates the introduction into

TABLE III. *New values of the wave-lengths of several lines and of the absorption limits in the L-series of Au(79).*

Line	β_2 [1]	β_3	β_{15}	γ_6 [1]	γ_2	γ_8	L_{II}
Drum reading	1068.42	1066.24	1070.10	901.6	902.8	908.5	900.9
Correction	−0.41	−0.41	−0.41	−0.6	−0.6	−0.6	−0.6
	1068.01	1065.83	1069.69	901.0	902.2	907.9	900.3
Siegbahn	1068.01	1065.50	1069.90	901.0	902.48	907.9	900.9

Line	(γ_4, γ_4')	γ_4	γ_4'	L_{I}	β_5 [1]	L_{III}
Drum reading	866.2	865.8	866.85	862.0	1038.76	1038.46
Correction	−0.7	−0.7	−0.7	−0.7	−0.76	−0.76
	865.5	865.1	866.15	861.3	1038.00	1037.7
Siegbahn	865.5			862.2	1038.00	1038.2

[1] Siegbahn's value (*Spektroskopie der Roentgenstrahlen*) taken as standard of reference.

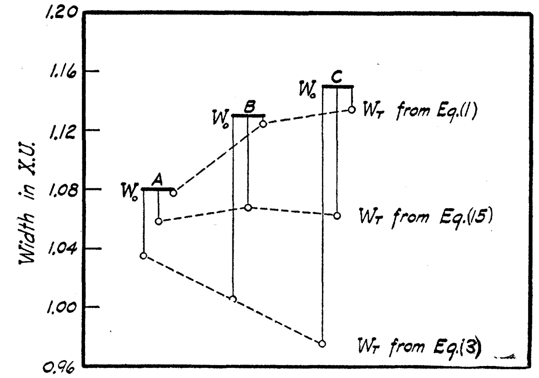


FIG. 9. Showing graphically the superiority of the empirical Eq. (15) as a method of correcting for the crystals.

Eq. (16) of rather elaborate corrections,[33] unless the two lines do not differ greatly in wave-length. We have not felt justified in departing far enough from the main object of this investigation to make measurements for and to determine these corrections. However, for lines that do not differ greatly in wave-length Eq. (16) may be used as a first approximation. Accordingly, using Eq. (16) we have computed the relative intensities of the lines in each of several arbitrarily selected groups, the lines in any group being close enough together so that we have neglected the corrections referred to above. The intensity of the strongest line in each group is arbitrarily set at 100. Values of a are taken from Figs. 3; of b_λ from column 5 of Table II ($2b_\lambda = W_O$). The various values of R are given in Table II, column 4.

We have also recorded the intensities of the satellites of $L\alpha_1$ and $L\beta_2$. The $L\alpha$ satellites have an intensity of 5 percent of that of the parent line; the corresponding value for the $L\beta_2$ satellites is 5.5 percent.

V. THE WIDTHS OF ABSORPTION LIMITS AND ENERGY LEVELS

One test of the relation between the widths of lines and energy levels given by Eq. (11) is afforded by the data in Table II. Two lines which have a common final level but different initial levels should differ in width by the difference between the widths of the initial levels. For example, for the respective widths of the lines α_2 and β_1 Eq. (11) predicts

$$W_{\alpha_2} = \Gamma_{L_{\text{III}}} + \Gamma_{M_{\text{IV}}}; \quad W_{\beta_1} = \Gamma_{L_{\text{II}}} + \Gamma_{M_{\text{IV}}}.$$

Therefore $W_{\alpha_2} - W_{\beta_1} = \Gamma_{L_{\text{III}}} - \Gamma_{L_{\text{II}}}$. The several pairs of lines which give the difference in width between L_{III} and L_{II}, and the differences so predicted, are given in the upper half of Table IV.

TABLE IV. *Differences in width between the L energy levels of Au(79).*

Lines	$l-\eta$	$\alpha_2-\beta_1$	$\beta_6-\gamma_5$	$\beta_{15}-\gamma_1$	$\beta_7-\gamma_8$
Width V (volts)	19.8−19.3	8.5−7.75	16.3−15.2	11.0−10.8	13.1−9.5
ΔV for $L_{\text{III}}-L_{\text{II}}$ (volts)	0.5	0.75	1.1	0.2	3.6
Lines	$\beta_9-\alpha_1$	$\beta_{10}-\alpha_2$			
Width V (volts)	12.1−8.1	13.1−8.5			
ΔV for $L_{\text{I}}-L_{\text{III}}$ (volts)	4.0	4.6			

Considering the difficulty in determining the widths of β_{15}, β_7 and γ_8 (see Figs. 3 and 6) not too much dependence should be put on the last two values. It is believed therefore that the table shows no significant variation from constant value for the difference $L_{\text{III}}-L_{\text{II}}$. The values given for the widths of α_2 and β_1 are probably more accurate than are those of the other lines; hence 0.75 volt is thought to be the best value for the difference in width of the states L_{III} and L_{II} of Au(79).

The lower half of Table IV contains two values for the difference $L_{\text{I}}-L_{\text{II}}$, the mean of which may be taken as 4.3 volts. Combining this with the value 0.75 for the difference $L_{\text{III}}-L_{\text{II}}$ we obtain 5.1 volts for the difference $L_{\text{I}}-L_{\text{II}}$.

The data in Table IV are thus in substantial agreement with Eq. (11). Although absolute values for the widths of the several L energy states are not obtainable from these data, it is to be noted that L_{I} is several volts wider than either L_{II} or L_{III}; and that these latter differ from each other in width by less than a volt, a conclusion in agreement with the authors' observation[4] that the $K\alpha$ lines of W(74) differ from each other in width by less than a volt.

As pointed out above, if the width of one energy state can be determined from an analysis of the observed shape of an absorption limit, one can, by use of Eq. (11) and the values of W_T for the L lines as given in Table II, determine the

---

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

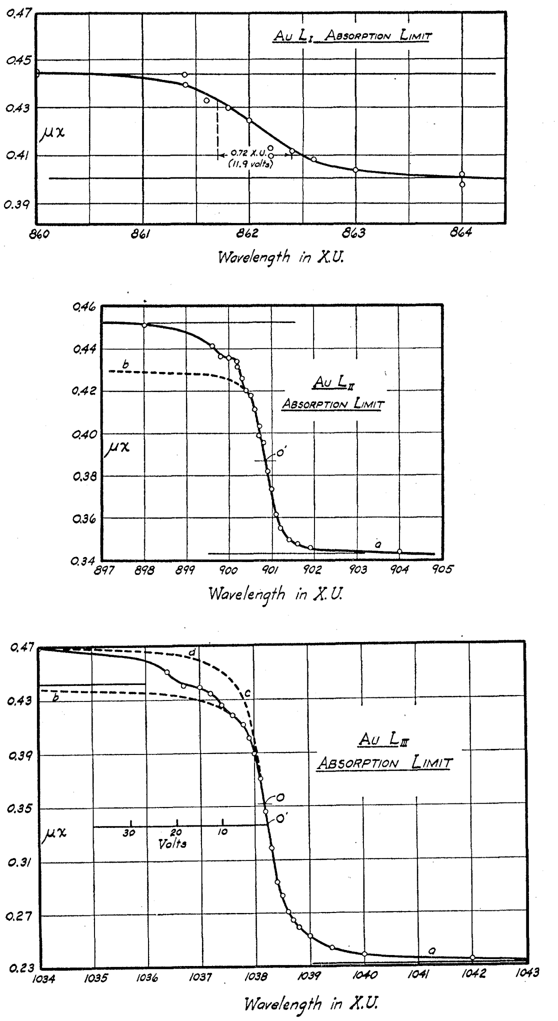


FIG. 10. (a) The L_I absorption discontinuity of Au(79).
(b) The L_{II} absorption discontinuity of Au(79). The circles are observed points. The smooth curve a $O'b$ is an arctangent curve adjusted to fit the main absorption edge with center at O'.
(c) The L_{III} absorption discontinuity of Au(79). The circles are the observed points. The dotted line $aO'b$ is an arctangent curve fitted to the main absorption edge with center at O'. The dotted curve Ocd is the "reversed mirror image" of the lower half of the observed curve, plotted from O as a center, point O being halfway between the upper and lower asymptotic values.

widths of the several L, M, N and O levels. Accordingly, by use of a platinum-target tube, careful measurements were made of the L_I, the L_{II} and the L_{III} limits of gold. The observations are shown graphically by the circles in Figs. 10(a), (b) and (c). The data[34] on L_I should be regarded as only roughly quantitative, so far as yielding the width of the L_I energy state. The data on L_{II} and particularly L_{III} are much better. Even neglecting the "humps" on the short wave-length side of L_{II} and L_{III} the discontinuity is not symmetrical, as may be seen from the dotted curve bc in Fig. 10(c), which is the reversed mirror image of the lower half of the observed curve plotted from O, which is halfway between the upper and the lower asymptotic values of the curve.

We now have the difficult problem of interpreting these data so as to determine therefrom the value of Γ, the energy level width. There are at least two possibilities: (1) We may regard the L_{III} discontinuity (L_{II} or L_{III} as shown in Fig. 10(b) and (c)) as made up of a "main" discontinuity, upon the short wave-length side of which are two secondary discontinuities, the origin of which is not explained and which cause the "humps," separated some 10 and 20 volts, respectively, from the center of the main edge. If we further adopt the assumptions upon which Eq. (13) is based (equal distribution of energy levels at the periphery of the atom) this main edge should follow an arctangent curve. Such a curve $aO'b$ plotted from O' as a center is fitted to this main edge. The agreement with the observations is seen to be excellent particularly on the long wave-length side of the edge. The "observed" width of the L_{III} energy level (see explanation following Eq. (13)) as obtained from this arctangent curve is 6.5 volts for the L_{II} level and 5.1 volts for the L_{III} level. These values must be corrected for the effect of the crystals.

Since as explained above (Fig. 1) the arctangent curve is the envelope of a series of overlapping, equal and equally spaced absorption lines, the width of each such line is 6.5 volts for L_{II} and 5.1 volts for L_{III}. After correcting for the (1, -1) rocking curve of the crystals by use of Eq. (15) just as correction is similarly made for an emission line, we have for the *true* width Γ of the L_{II} level 5.8 volts; and for the L_{III} level 4.4 volts. According to these directly observed values, the L_{II} level should be wider than the L_{III} level by about 1.4 volts; whereas from the

---

[34] The values of μ($\mu \equiv$absorption coefficient) are not corrected for higher orders of radiation present in the incident beam. This correction if made would change the absolute magnitude of μ but not the *form* of the curves in Figs. 10.

data in Table IV we saw that the reverse should be true: that the L_{III} level should be wider by about 0.7 volt. We think that this discrepancy between the difference in widths obtained from line data and from the direct observations on limits is outside experimental error; but we are unable to explain the cause thereof.

Since the L_{III} data are the more precise, we think that the value for it—4.4 volts—is more reliable. Accordingly we take that value as a starting point and proceed, by use of Eq. (11) and the line-width data of Table II, to determine the widths of the several L, M, N and O states. The results are shown in Table V. (The emission line the width of which is combined with that of the appropriate L level to give the width in question, is given in brackets.)

TABLE V. *The widths of the x-ray energy levels of Au(79).*

Level	Quantum numbers		Level width computed from	Level width (volts)
K	$n=1, l=0$		[4]	40
L_{I}	2	0	See Table IV	8.7
L_{II}	2	1	See Table IV	3.7
L_{III}	2	1	[1]	4.4
M_{I}	3	0	$\eta-L_{\mathrm{II}}$, $l-L_{\mathrm{III}}$	15.6, 15.4
M_{II}	3	1	β_4-L_{I}	10.7
M_{III}	3	1	β_3-L_{I}	12.1
M_{IV}	3	2	β_1-L_{II}, $\alpha_2-L_{\mathrm{III}}$, $\beta_{10}-L_{\mathrm{I}}$	4.0, 4.1, 4.4
M_{V}	3	2	$\alpha_1-L_{\mathrm{III}}$, β_9-L_{I}	3.7, 3.4
N_{I}	4	0	γ_5-L_{II}, β_6-L_{III}	11.5, 11.9
N_{II}	4	1	γ_2-L_{I}	8.5
N_{III}	4	1	γ_3-L_{I}	6.5
N_{IV}	4	2	γ_1-L_{II}, $\beta_{15}-L_{\mathrm{III}}$	7.1, 6.6
N_{V}	4	2	β_2-L_{III}	5.9
$N_{\mathrm{VI, VII}}$	4	3	$\beta_7'-L_{\mathrm{III}}$	5.4
O_{I}	5	0	β_7-L_{III}, γ_8-L_{II}	8.7, 5.8
O_{II}	5	1	γ_4-L_{I}	9.9
O_{III}	5	1	$\gamma_4'-L_{\mathrm{I}}$	9.9
O_{IV}	5	2	γ_6-L_{II}	4.4
O_{V}	5	2	β_5-L_{III}	3.2

[1] Determined from observation on L_{III} absorption limit and taken as a starting point for computing the other levels.

However, the assumptions upon which Eq. (14) are based (Fermi-Sommerfeld distribution of energy levels in a metal) should be more applicable to gold than are the assumptions underlying Eq. (13). As was mentioned above, Eq. (14) predicts an asymmetrical limit, the curvature being less on the short wave-length side. An inspection of the data shown in Figs. 10(b) and 10(c) shows that, except for the humps, both L_{II} and the L_{III} limits have exactly this type of asymmetry. To test Eq. (14) the necessary constants were chosen by trial and error so as to get the best fit between the equation and experiment. The results are shown in Figs. 11 and 12 for the L_{II} and the L_{III} limits, respectively. For the L_{II} limit, the width Γ of the L_{II} level was assumed to be 7.0 volts, which corrected for the crystals, becomes 6.3 volts. For the L_{III} limit the corresponding assumed width was 5.3 volts, corrected to 4.6 volts. However, to make the curves fit, it was necessary to assume a value for ν_i (see page 846) of 100 volts, instead of 10 volts normally to be expected for the gold lattice. The source of this discrepancy is not obvious.

Again we assume that the greater accuracy of the L_{III} data gives preference to the value of 4.6 volts for the width of the L_{III} energy level, as a starting point for the determination of the remaining levels. This value is within experimental error equal to that obtained from the arctangent curve—4.4 volts. Hence Eq. (14) predicts substantially the same set of energy levels as does Eq. (13).

Only a rough estimate of the width of the L_{I} limit can be obtained from Fig. 10(a); but the curve seems to give a somewhat greater width for the L_{I} level than predicted in Table V.

Some significant regularities in the values obtained for the widths of these energy states are to be noted. (1) In any given series of levels—L, M . . . —the width decreases with increasing value of the orbital quantum number l. Exceptions to this rule, found in the N and the O levels, may be due to experimental error. (2) Energy states having the same total quantum number n

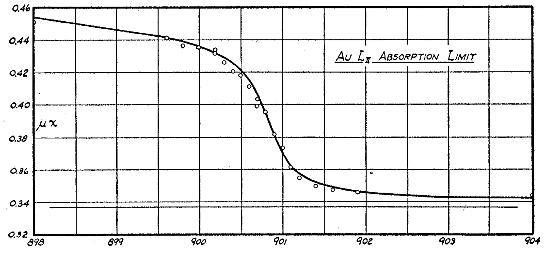


FIG. 11. The L_{II} absorption discontinuity of Au(79). The circles are observed data. The curve is a plot of Eq. (14) for $\nu_i=100$ volts and $\Gamma=7.0$ volts.

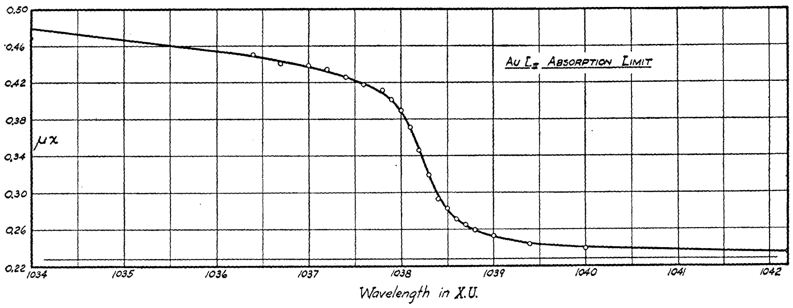


FIG. 12. The L_{III} absorption discontinuity of Au(79). The circles are observed data. The curve is a plot of Eq. (14) for $\nu_i = 100$ volts and $\Gamma = 5.3$ volts.

and orbital quantum number l have nearly the same width. This is in agreement with the authors' observations[4] that the components of any given K doublet of W(74) have nearly identical widths. (3) Except for the L_I level, the widths of levels for which $l=0$ decrease in width with increasing value of n. The K level $(n, l=1, 0)$ may be included in this statement. We have no accurate direct measurements on the width of the K-limit of Au(79) but we may make a reasonable estimate of it. The authors have reported[4] that the width of the lines $K\alpha_{1,2}$ of W(74) is about 43 volts; and of the $K\beta$ lines about 48 volts. Making the reasonable assumption that the widths of $L_{II, III}$ and of the $M_{II, III}$ levels of W(74) are not very different from those of Au(79), we conclude that the width of the K level Au(79) should be of the order of 40 volts.

Within any given series, these regularities are in agreement with the rule proposed by Coster[35] that energy levels are sharper the smaller the value of n/k, where n is the total quantum number and $k(=l+1)$ is the azimuthal quantum number. From one series to another, however, Coster's rule does not seem to apply.

Several bits of evidence may be cited to confirm more or less qualitatively the general correctness of the values given in Table V, for the several energy-level widths.

(1) The authors have shown[4] that the components of the $K\beta$ doublet of W(74) are some 6 volts wider than those of the $K\alpha$ doublet. The data in Table V predict that the $K\beta$ lines of Au(79) should be some 7 volts wider than for $K\alpha$. However, from Table V one would also predict that the $K\gamma$ lines of gold should be wider than the $K\alpha$ lines. The opposite was found to be the case for W(74). This discrepancy may mean either that the underlying theory of the relation of the widths of lines and energy levels is incomplete; or that the width assumed for the L_{III} level is incorrect.

(2) Siegbahn[36] gives the widths of several of the M lines of Au(79) based on measurements by Molin. Although uncorrected for the error due to the crystals used, these values cannot be far from the true widths. They are given in column 3 of Table VI. The values predicted for these same line widths by use of the level widths given in Table V (column 4) are given in the last column of Table VI. The agreement is seen to be reasonably good.

TABLE VI.

		Full width at half-maximum	
Line	Transition	Siegbahn	Computed from Table V, column 4
$M\alpha_1$	$M_V \rightarrow N_{VII}$	5.0 volts	9.0 volts
$M\gamma$	$M_{III} \rightarrow N_V$	17.0	18.0
—	$M_{III} \rightarrow N_I$	20.0	23.8

APPENDIX

DERIVATION OF EQ. (12) OF TEXT

According to Eq. (12) the total probability of absorption of a quantum $h\nu$ is given by the sum of the probabilities of such an absorption involving the change of state of the atom from the normal state (A) to a particular state E. In

---

[35] D. Coster, Zeits. f. Physik **45**, 797 (1927).

[36] *Spektroskopie der Roentgenstrahlen*, 2d Ed., p. 367.

other words, supposing that the energy levels E are discrete (due to the introduction of a fictitious high potential wall surrounding the atom or crystal which we are considering), Eq. (12) tells us that the absorption curve for the limit results from the additive superposition of the absorption lines corresponding to the individual states E. Now Weisskopf and Wigner[37] have demonstrated by examples that transition probabilities (and hence, in particular, absorption probabilities) from the same initial state to a group of other (excited) states are simply additive under the condition that the final state of the atom and the radiation field[38] is necessarily different for every one of the excited states. Normally this is not so, even if the excited states have different energy. For if they lie very closely together, differing, e.g., in term value by less than the width of the absorption line corresponding to excitation to a single level, it is perfectly possible that the atom may pass from the normal state back to the normal state by way of different excited states with the absorption and emission of an identical group of photons (due to the overlapping of the several absorption and emission lines). In the following we shall try to show that, in the case we are considering, we can eliminate this possibility by slightly altering the problem through the introduction of certain artificial assumptions. To the modified problem we can then adapt Weisskopf and Wigner's calculations and, for it, derive formula (12) of the text.

Consider an atom initially in the normal state in a radiation field of given density and spectral distribution,[39] $\Sigma_s n_s h\nu_s$. Let the probability that the system (atom plus field) is in this condition be given by $|a_A|^2$, a_A being the so-called probability amplitude of the initial state. As time goes on, a probability develops that the atom has absorbed a quantum $h\nu_\rho$ from the radiation field, leaving the atom in the excited state E; let the probability amplitude for this latter condition be $a_E{}^\rho$. Simultaneously, probabilities for the existence of other states arise, corresponding to the emission of fluorescent radiation.[40]

To make the treatment as simple as possible without losing sight of the characteristic features of the problem, let us suppose that the return of the atom to the normal state from state E takes place in three stages, $E\rightarrow B\rightarrow C\rightarrow A$, with the emission of the photons $h\nu_\sigma$, $h\nu_\tau$ and $h\nu_\omega$, such that $\nu_\sigma \gg \nu_\tau \gg \nu_\omega$, in this succession. Let the first two steps involve a readjustment of the inner shells only and the last the return of the ejected electron to the residual vacancy, which can be assumed to be in one of the outermost occupied shells of the atom. We will also consider a second probability, i.e., that the atom is excited by absorption of radiation of frequency ν_ρ' to the state immediately above E in the sequence of energy levels, E',[41] and returns to the normal state by way of the states B' and C' with the emission of radiation of frequency ν_σ', ν_τ' and ν_ω'. Again we suppose the ejected electron not to alter its quantum state before the atom, by the transitions involving the emission of the photons $h\nu_\sigma'$ and $h\nu_\tau'$, has transferred most of its energy to the radiation field.[42] The two series of transitions are represented in Fig. 13. With the above assumptions we can be certain that the term separation $|\nu_{C'}-\nu_C|$ is at least of the same order of magnitude as $|\nu_{E'}-\nu_E|$. On the other hand, we know that, since the atomic state C corresponds to a vacancy in one of the outermost shells of the atom, the widths of the state C and C' (Γ_C and $\Gamma_{C'}$) are extremely small (approaching those for optical levels) compared with those of the states E and E' ($\Gamma_E \backsimeq \Gamma_{E'}$). To be able to apply the calculations of Weisskopf and Wigner (reference 6, p. 67) directly to our problem we now make use of the following device: We adjust the dimensions of our fictitious shell of high potential around the atom until the separations between the successive levels E, E', etc., satisfy the following relation: $\Gamma_E \gg |\nu_{E'}-\nu_E| \gg \Gamma_C$ and therefore also $|\nu_{C'}-\nu_C| \gg \Gamma_C$. As the probability of emission of a quantum of frequency ν_ω is appreciable only when ν_ω differs from $(\nu_C-\nu_A)$ by a quantity not materially greater than Γ_C, this means that the ranges for which the probabilities of emission of $h\nu_\omega$ and $h\nu_{\omega}'$ are other than negligible, are well separated. On the other hand, in view of the smallness of Γ_C referred to the resolving power of the spectrometer, the introduction of the high potential wall of the required dimensions may be assumed not to alter the structure of the absorption limit to an observable extent. The introduction of this fictitious shell of perfectly definite dimensions and the exclusion of a number of possible transitions of low probability constitute the artificial changes which we have to make in the real problem in order to make Weisskopf and Wigner's calculations applicable and hence to derive our formula for the absorption coefficient.

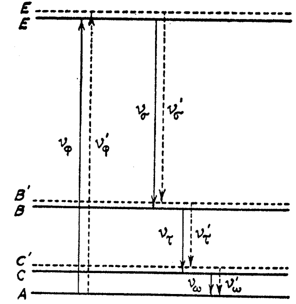


FIG. 13. Schematic diagram of transitions involved in the excitation of an atom by absorption of a photon and its subsequent return to the normal state.

---

[37] V. Weisskopf and E. Wigner, Zeits. f. Physik **63**, 67 (1930).

[38] In our case this is the normal state of the atom and the initial state of the radiation field minus the photons absorbed in the process of excitation and plus those emitted during the return of the atom to the normal state.

[39] We think of the atom, including the high potential wall, and the radiation field as enclosed in a large box with perfectly reflecting walls. It is then possible to describe any radiation field in the interior in terms of a discrete set of standing waves of frequency ν_S and energy $n_S h\nu_S$, where n_s is an integer. See, e.g., E. Fermi, Rev. Mod. Phys. **4**, 87 (1932).

[40] The change with time in the several probability amplitudes is due to the interaction of the atom and the radiation field and governed by the time-dependent Schrödinger equation (Weisskopf and Wigner, Zeits. f. Physik **63**, 54 (1930), Eq. (12)). The purpose of the present considerations is to show that certain solutions of this equation found by Weisskopf and Wigner for particular cases can be applied directly to the problem of x-ray absorption in the neighborhood of a limit if certain simplifications are introduced.

[41] For the present we consider only a single sequence of terms, i.e. terms corresponding to a single set of angular quantum numbers.

[42] This excludes the possibility that the states B and C may be identical with B' or C'.

We have now achieved that the final state with the probability amplitude[43] $a^{\rho}{}_{A\sigma\tau\omega}$ can be reached by one path only, i.e., by the series of transitions $A\rightarrow E\rightarrow B\rightarrow C\rightarrow A$, even though the possible values of ν_ρ, ν_σ and ν_τ may overlap with those of ν_ρ', ν_σ' and ν_τ'. The same is true for any other final state, such as that with the probability amplitude $a^{\rho'}{}_{A\sigma'\tau'\omega'}$. This is the condition for the application of Weisskopf and Wigner's calculation to the problem of finding the value of the relative probability that, after a long time has elapsed,[44] the atom has absorbed radiation of frequency between ν_ρ and $\nu_\rho+d\nu_\rho$, and emitted radiation quanta of frequency between ν_σ and $\nu_\sigma+d\nu_\sigma$, ν_τ and $\nu_\tau+d\nu_\tau$, and ν_ω and $\nu_\omega+d\nu_\omega$. This is equal to:[45]

$$\lim_{t\rightarrow\infty}\sum_{\nu_\rho}^{(\nu_\rho+d\nu_\rho)}\ \sum_{\nu_\sigma}^{(\nu_\sigma+d\nu_\sigma)}\ \sum_{\nu_\tau}^{(\nu_\tau+d\nu_\tau)}\ \sum_{\nu_\omega}^{(\nu_\omega+d\nu_\omega)} |a^{\rho}{}_{A\sigma\tau\omega}|^2 = J(\nu_\rho,\ \nu_\sigma,\ \nu_\tau,\ \nu_\omega)d\nu_\rho d\nu_\sigma d\nu_\tau d\nu_\omega$$

$$= \frac{\nu_\rho}{\nu_{EA}}\frac{\nu_\sigma}{\nu_{EB}}\frac{\nu_\tau}{\nu_{BC}}\frac{\nu_\omega}{\nu_{CA}}\frac{(1/\nu_\rho)f(\nu_\rho)(\gamma_{EA}/2\pi)d\nu_\rho}{(\Gamma_{A/2})^2+(\nu_\rho-\nu_\sigma-\nu_\tau-\nu_\omega)^2}$$

$$\frac{(\gamma_{EB}/2\pi)d\nu_\sigma}{(\Gamma_{E/2})^2+(\nu_{EA}-\nu_\sigma-\nu_\tau-\nu_\omega)^2}\ \frac{(\gamma_{BC}/2\pi)d\nu_\tau}{(\Gamma_{B/2})^2+(\nu_{BA}-\nu_\tau-\nu_\omega)^2}\ \frac{(\gamma_{CA}/2\pi)d\nu_\omega}{(\Gamma_{C/2})^2+(\nu_{CA}-\nu_\omega)^2}.$$

Finally we obtain for the total probability that a quantum of frequency between ν_ρ and $\nu_\rho+d\nu_\rho$ has been absorbed, summing over all states E,

$$J(\nu_\rho)d\nu_\rho = \sum_{\nu_E=\nu_{E_0}}^{\nu_E=\infty}(E)\int_{\nu_{EB}-\Delta\nu_\sigma}^{\nu_{EB}+\Delta\nu_\sigma} d\nu_\sigma \int_{\nu_{BC}-\Delta\nu_\tau}^{\nu_{BC}+\Delta\nu_\tau} d\nu_\tau \int_{\nu_{CA}-\Delta\nu_\omega}^{\nu_{CA}+\Delta\nu_\omega} d\nu_\omega\ J(\nu_\rho,\ \nu_\sigma,\ \nu_\tau,\ \nu_\omega)d\nu_\rho$$

$$= \sum_{\nu=\nu_{E_0}}^{\nu_E=\infty}(E)\frac{f(\nu_\rho)}{\nu_{EA}}\frac{\gamma_{EA}}{\Gamma_A}\frac{\gamma_{EB}}{\Gamma_E}\frac{\gamma_{BC}}{\Gamma_B}\frac{\gamma_{CA}}{\Gamma_C}\frac{(\Gamma_A+\Gamma_E/2\pi)d\nu_\rho}{((\Gamma_A+\Gamma_E)/2)^2+(\nu_{EA}-\nu_\rho)^2}.$$

Here $f(\nu_\rho)$ gives the spectral distribution of intensity of the incident beam.[46]

Here $\Delta\nu_\sigma$, $\Delta\nu_\tau$, $\Delta\nu_\omega$ are frequency intervals large compared with Γ_E, Γ_B, Γ_C, respectively, so that the range of integration covers the region where the integrand is not negligible. Furthermore an inspection of the calculation of Weisskopf and Wigner shows that if we would take into consideration all the possible cascaded transitions from state E to the normal state[47] the factor $(\gamma_{EB}/\Gamma_E)(\gamma_{BC}/\Gamma_B)(\gamma_{CA}/\Gamma_C)$ would have to be replaced by unity. This is of course evident if the only possible transitions from the states E, B and C are just $E\rightarrow B$, $B\rightarrow C$ and $C\rightarrow A$, respectively. Furthermore, we may, without causing an appreciable error, replace ν_{EA} in the multiplying factor by ν_ρ. If we finally consider the fact that the life of the normal state in the radiation field is extremely long compared with that of an excited state E, i.e., $\Gamma_A \ll \Gamma_E$, and also that the absorption coefficient is given by the product of the probability of absorption of a quantum from a beam of unit intensity and of the energy of the quantum, we arrive at our Eq. (12) for the partial absorption coefficient $K(\nu)$:

$$K(\nu) = C\sum_{\nu_{EA}=\nu_{E_0A}}^{\nu_{EA}=\infty}(E)\ \gamma_{EA}\left(\frac{\Gamma_{E/2\pi}}{(\nu_{EA}-\nu)^2+(\Gamma_{E/2})^2}\right).$$

We must still discuss the effect of the existence of several sequences of energy levels, corresponding to different angular quantum numbers. Wentzel[48] has shown that the degeneracy resulting from the existence of different magnetic states of equal energy produces no difficulties as long as we confine ourselves to dipole absorption; then the transition probabilities of the several degenerate states simply add up. We know that with x-rays of about 1A wave-length the quadrupole absorption is not negligible, but yet far less than the dipole absorption, so that the effect of the former on the shape of the absorption limit can be at most very slight. We cannot dispose as easily of the case that there are coincident states E with different j-values and azimuthal quantum numbers. In this case, however, the different selection and intensity rules make it extremely likely that the return to the normal state will take place by different routes (with the emission of quanta of different frequency). Under these circumstances we can apply the method of Weisskopf and Wigner as before.

---

[43] We indicate by the upper index the absorbed quantum, by the lower indices the state of the atom and the emitted quanta. We exclude from consideration the possibility of repeated absorption by the same atom as this is very improbable during the short period of excitation and cannot change the results if it takes place after the atom has returned to the normal state.

[44] The time should be long compared to the mean lives of the atomic states involved.

[45] V. Weisskopf and E. Wigner, reference 11, Eq. (29a).

[46] G. Wentzel, Handb. d. Physik **24**, Part 1, 756 (1933).

[47] The exclusion of certain of these, such as the direct transition $E\rightarrow A$, to make the method applicable, plays a minor rôle, as their relative probability is small.

[48] G. Wentzel, reference 46, p. 757.