

A NEW TYPE OF AUGER EFFECT AND ITS INFLUENCE ON THE X-RAY SPECTRUM

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Summary

It is pointed out that the radiationless transition $L_I \rightarrow L_{III}$ with simultaneous ejection of an outer electron is of great importance in the interpretation of several features in the X -ray spectra, hitherto unexplained. It is responsible for the abnormal weakening of the emission lines with L_I as initial level (§ 1); the large intensity of the L_{III} -satellite lines within certain ranges of atomic number both for cathode ray and fluorescent excitation (§ 2); the greater diffuseness of the L_I -emission lines as compared with the L_{II} , L_{III} -emission lines (§ 3). It seems reasonable to assume that in the M -region similar radiationless transitions occur with analogous results.

Introduction. The experimental and theoretical investigations of the last twenty years have led to an interpretation of the X -ray spectra which covers in a satisfactory way almost all the details actually observed. Only a few features remain, regarding which an explanation is still outstanding. In the first place it appears that the relative intensity of the X -ray emission lines is not always in accordance with the simple expectation. This effect is most noticeable in the case of the L -emission lines, where there is strong evidence that the transitions with L_I as initial level are weaker in comparison to those with L_{II} and L_{III} as initial levels than one would predict on the basis of the radiative transition probabilities. Another phenomenon requiring elucidation is the abnormally great intensity of the satellite lines in the L -series, observed especially for silver and the elements immediately preceding it in the periodic system, where it may amount to as much as half of that of the parent lines. It seems impossible to account for such a large ratio on the basis of the ordinary theory of spark excitation, according to which the satellite

lines arise from an atom that is doubly ionised by an electron impinging on the anticathode or by an incident X -ray quantum. This is the more curious since the behaviour of the satellites in the K -series is in agreement with the theory just mentioned. Finally there seems to exist a relationship between the diffuseness of the X -ray levels and their azimuthal quantum number l , in the sense that for the levels differing only in the value of l the diffuseness decreases with increasing l , so that e.g. the levels L_{II} and L_{III} with $l = 1$ are sharper than the level L_I with $l = 0$. In the following paragraphs we shall attempt to arrive at an understanding of all these phenomena by means of a very simple and plausible assumption.

§ 1. *The Abnormal Weakness of the L_I -Emission Lines.* Some time ago W o l f¹⁾ has investigated the oscillator strength of the X -ray transitions involving the $2s$ - and the $2p$ -electrons. The $2s$ -electrons give rise to the L_I -absorption band, the $2p$ -electrons to the L_{II} - and L_{III} -absorption bands. From the dependance of the absorption coefficient upon the frequency, as computed from theory by S t o b b e²⁾, and from his own measurements near the absorption edges W o l f could obtain the total oscillator strengths f_{cont} of these continuous absorption bands. His results are given in table 1.

TABLE I
Oscillator strength for the transitions of the $2s$ - and the $2p$ -electrons.

2s					2p			
	f_{cont}	f_{em}	f_{abs}	Σf	f_{cont}	f_{em}	f_{abs}	Σf
with data of W o l f								
<i>Ag</i>	1.3	—	0.2	1.5	4.01	—0.40	2.39	(6.00)
<i>Pt, Au</i>	1.3	—	0.2	1.5	3.86	—0.37	2.51	(6.00)
with data of H ö n l								
<i>Ag</i>	1.50	—	0.11	1.61	4.64	—0.40	1.76	(6.00)
<i>Pt, Au</i>	1.33	—	0.16	1.49	3.44	—0.37	2.93	(6.00)

The sum rule of K u h n, T h o m a s and R e i c h e³⁾ states that the total oscillator strength Σf of all radiative transitions which an electron moving in a constant field of force can make from a given

1) M. W o l f, Ann. d. Phys. **16**, 973, 1933; Dissertation Groningen 1933.

2) M. S t o b b e, Ann. d. Phys. **7**, 661, 1930.

3) W. K u h n, Zs. f. Phys. **33**, 408, 1925; W. T h o m a s, Naturw. **13**, 627, 1925; F. R e i c h e and W. T h o m a s, Zs. f. Phys. **34**, 510, 1925.

stationary state to other stationary states is equal to unity. Since in the interior of the atom the electrons may be approximately treated as moving independantly in a central field of force, we should expect for the $2s$ - and the $2p$ -electrons total oscillator strengths 2 and 6 respectively, there being two $2s$ -electrons and six $2p$ -electrons. As first explained by K r o n i g and K r a m e r s ¹⁾ in the case of the K -absorption band, the difference between these values and the values f_{cont} mentioned above must be ascribed to the circumstance that the individual electrons in the atom cannot make all the transitions possible for them if each one were present alone, the exclusion principle preventing them to go over to stationary states already occupied by other electrons. In applying the sum rule we must hence include the oscillator strengths of these prohibited transitions, to be counted negative in the case of emission and positive in the case of absorption.

This may be done as follows: A $2s$ -electron, if present alone in the central field of the atom, can make no emissive transitions; a $2p$ -electron on the other hand can make the transitions $2p \rightarrow 1s$ and $2p \rightarrow 2s$. The oscillator strength f_{em} of the first transition can according to W o l f be estimated by taking as the oscillator strength of all the transitions ending upon $1s$ the difference of about 0.5 between the total oscillator strength 2 of the K -electrons and the oscillator strength of the K -absorption band; and by ascribing to the transition $2p \rightarrow 1s$ such a fraction of this difference as corresponds to the intensity ratio between the emission line $K\alpha$ and the other K -emission lines. The second transition may be disregarded, its small frequency causing its f -value to be negligible too. In order to obtain the values f_{abs} of the transitions which the $2s$ - and $2p$ -electrons could perform to the higher discrete stationary states of the atom if these were not occupied, W o l f considers the inverse processes, viz. the transitions in which the outside electrons fall into a vacant place in the group of $2s$ - or $2p$ -electrons. These transitions give rise to the L -series in the X -ray emission spectrum. As the ratio of the values f_{abs} for the $2s$ - and the $2p$ -electrons W o l f takes the ratio of the total intensities of all emission lines with the initial state L_I (vacancy in the group of $2s$ -electrons) and with the initial states L_{II} - or L_{III} (vacancy in the group of the $2p$ -electrons) after multiplication with

1) R. de L. Kronig, and H. A. Kramers, Zs. f. Phys. **40**, 174, 1928.

the inverse cube of the frequencies in order to reduce them to oscillator strengths. Not knowing the absolute values of f_{abs} , this quantity was chosen for the $2p$ -electrons in such a way as to make $\Sigma f = f_{cont} + f_{em} + f_{abs}$ for them equal to 6. The quantity f_{abs} for the $2s$ -electrons being thereby also determined, we can now calculate Σf for them. We find then a value noticeably smaller than 2, as shown by table 1.

Instead of employing for f_{cont} the semi-empirical data given by Wolf, we may also use values obtained purely from theory. f_{cont} for the L -absorption bands has thus been calculated by Hönl¹⁾ for various atomic numbers, and an interpolation of his results gives the second set of values f_{cont} in table 1. Applying for f_{em} and f_{abs} the method described above, we find the remaining numbers in the lower half of table 1, showing that the conclusions regarding Σf for the $2s$ -electrons are not essentially modified.

In order to explain the discrepancy discussed, one will naturally inquire if perhaps radiationless transitions (Auger effects) may influence the intensity ratio of the emission lines. Indeed, if the chance that an atom leaves the state L_I by a radiationless transition is much greater than that it leaves the states L_{II} or L_{III} by a similar process and moreover is comparable to the chance of a radiative transition, then the radiative transitions starting from L_I will be weakened relative to those starting from L_{II} and L_{III} , causing an apparent deficit for Σf of the $2s$ -electrons in the above computation. However, the magnetic investigation of the Auger effect by Robinson²⁾, where an M -, N -, . . . electron falls into the vacancy of the L -shell while another M -, N -, . . . electron is ejected from the atom, seems to show that the probability of these radiationless transitions is much smaller in L_I than in L_{II} and L_{III} .

It is the purpose of this paper to point out that the assumption of radiationless transitions as the source of the discrepancy is quite correct, but that the Auger effect responsible is the one in which a transition $L_I \rightarrow L_{III}$ and the simultaneous ejection of an outer electron takes place, rather than the Auger effects previously mentioned. Due to the relatively small size of the energy difference $L_I - L_{III}$ the ejected electrons in general are quite slow, and this

1) H. Hönl, Zs. f. Phys. **84**, 1, 1933.

2) H. R. Robinson and A. M. Cassie, Proc. Roy. Soc. **113**, 282, 1927; H. R. Robinson and C. L. Young, Proc. Roy. Soc. **128**, 92, 1930.

probably is the reason why they have not been observed in Robinson's experiments. The chance for the process described taking place, on the other hand, must be especially great in some cases, as will appear from the evidence to be discussed presently. In this respect the radiationless transition differs markedly from the radiative transition $L_I \rightarrow L_{III}$ (or $2p \rightarrow 2s$), which, as stated before, is very weak and has only been observed for a few elements.

The weakening of the X-ray emission lines involving L_I as initial state is particularly prominent for the light elements¹⁾. Thus O'Bryan and Skinner²⁾, investigating the L -spectra of Na , Mg , Al , Si , which are situated in the soft X-ray region, could not find them at all while the lines with L_{II} , L_{III} as initial state showed considerable intensities. The elements in question have a complete K - and L -shell and in addition one, two, three or four M -electrons respectively. The above authors suggest that the absence of the $L_I \rightarrow M$ emission lines in their investigation is due to the fact that *radiative* transitions $L_I \rightarrow L_{III}$ are much more probable, a $2p$ -electron falling into the vacant place $2s$ before an M -electron gets a chance to fall into this place. However they looked in vain for an emission line $L_I \rightarrow L_{III}$ which should have been observable with their apparatus. We wish, on the other hand, to ascribe the non-appearance of the L_I -emission lines to the great probability of *radiationless* transitions $L_I \rightarrow L_{III}$ with transfer of this energy difference to one of the M -electrons.

§ 2. *Satellites in the L-Series.* An atom originally in the state L_I will by the radiationless transition $L_I \rightarrow L_{III}$ be left in the state L_{III} with an additional vacancy in an outer shell on account of the ejection of an electron. The atom is hence in a condition to emit an L_{III} -satellite line rather than a line fitting into the ordinary scheme of X-ray levels. We shall now show that the intensity of the L_{III} -satellite lines actually observed with cathode ray excitation of the L -spectrum in many cases is due principally to this cause and not to double ionisation of the atom by an impinging electron.

The satellites in the L -series have first been studied extensively by Coster³⁾, while recently Richtmyer and his pupils⁴⁾

1) J. A. Prins, *Zs. f. Phys.* **77**, 478, 1932.

2) H. M. O'Bryan and H. W. B. Skinner, *Phys. Rev.* **45**, 370, 1934.

3) D. Coster, *Phil. Mag.* **43**, 1070; **44**, 546, 1922.

4) F. K. Richtmyer and R. D. Richtmyer, *Phys. Rev.* **34**, 574, 1929; R. D. Richtmyer, *Phys. Rev.* **38**, 1802, 1931.

have undertaken a more detailed investigation. The satellites to which most attention has been paid are those of the lines $L\alpha$ (transition $L_{III} \rightarrow M_{IV}, \nu$) and $L\beta_2$ ($L_{III} \rightarrow N_{IV}$). A survey of all the experimental material regarding them has been given by Richtmyer and Kaufman¹⁾. It shows that they are rather weak for atomic number $Z < 40$, that for higher Z they rapidly become stronger, attaining a maximum intensity relative to the parent lines near $Z = 47$ (Ag), whereafter the intensity suddenly diminishes, becoming zero for $Z = 53$. The peculiar behaviour in the region $Z = 40$ to $Z = 50$ had already been pointed out by Coster²⁾ and is illustrated in a particularly convincing way by the new quantitative intensity measurements of Miss Pearsall³⁾ for the satellites of $L\beta_2$ (see fig. 1). In the case of $L\alpha$ all the evidence, as discussed

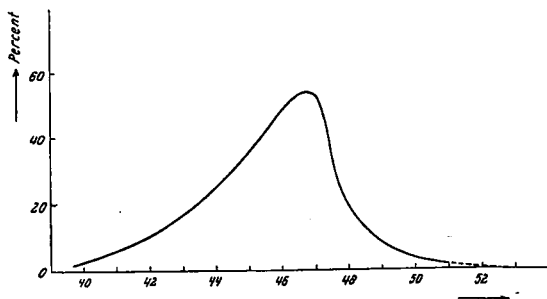


Fig. 1. Intensity of the satellites of $L\beta_2$ relative to the parent line as function of the atomic number.

by Richtmyer and Kaufman, points to the absence of satellites for atomic numbers $Z = 53$ to $Z = 74$ inclusive while for still higher atomic numbers they reappear. In the case of $L\beta_2$ no satellites are found for $Z = 53$ to $Z = 67$. For $Z = 68$ Coster reports a single satellite $L\beta'_2$. This satellite according to Richtmyer and Kaufman persists for the heavier elements. According to them a second satellite $L\beta''_2$ makes its appearance with faint intensity for $Z = 73$ while Kaufman⁴⁾ in addition finds satellites β_2^{III} , β_2^{IV} , β_2^V , β_2^{VI} , β_2^{VII} , first appearing respectively at $Z = 73, 74, 77, 74, 74$.

1) F. K. Richtmyer and S. Kaufman, Phys. Rev. **44**, 605, 1933.

2) D. Coster, Phil. Mag. **43**, 1070, 1922; see p. 1090.

3) A. W. Pearsall, Phys. Rev. **46**, 694, 1934.

4) S. Kaufman, Phys. Rev. **45**, 385, 1934.

In fig. 2 we have plotted the energy difference $L_I - L_{III}$ as function of Z . This energy difference is in no case sufficient to cause the M -shell to be ionised into M_I or M_{II} by a radiationless process. Only for the few heaviest elements can ionisation take place in M_{III} . For M_{IV} and M_V , however, the situation is different. Since the ionisation of the M -shell must take place in an atom with a vacancy in the L -shell and a resulting increase of the effective nuclear charge for the M -electrons, one should compare the energy difference $L_I - L_{III}$ for atomic number Z with the ionisation energies M_{IV} and M_V for $Z+1$. These latter have accordingly also been plotted in fig. 2. The diagram

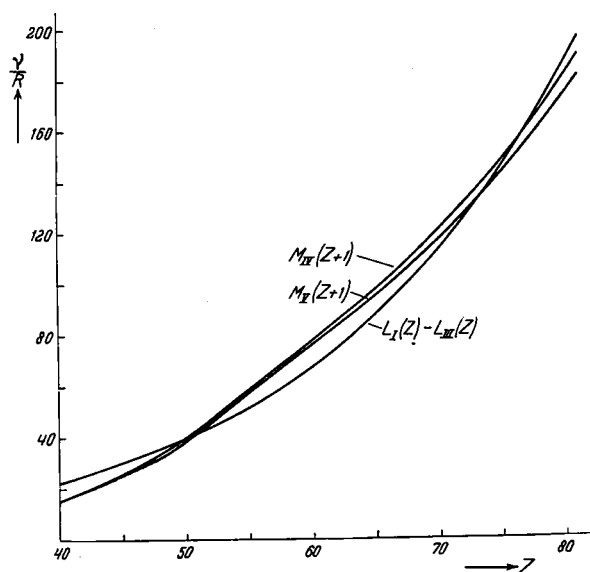


Fig. 2. Energy difference $L_I(Z) - L_{III}(Z)$ and energy $M_{IV}(Z+1)$ and $M_V(Z+1)$ as function of the atomic number.

shows that in the region where the satellites of $L\alpha$ and $L\beta_2$ are (practically) absent, $L_I - L_{III}$ is smaller than M_{IV} and M_V . We hence conclude that these satellites must be almost exclusively due to the Auger effect involving the transition $L_I - L_{III}$ with an accompanying ionisation of the M -shell into M_{IV} or M_V . The occurrence of the satellite $L\beta'_2$ at $Z = 68$ and above may be either due to true spark excitation or to Auger effects in which the N -shell is ionised.

A further confirmation of the view-point proposed is to be found in the great intensity of the satellites of $L\alpha$ and $L\beta_2$ in some cases. Thus for $Z = 47$ the intensity of the satellites of $L\beta_2$ is about 52 per cent of the intensity of the parent line (see fig. 1). Such a large ratio is quite impossible to explain on the assumption of direct double excitation while it fits in well with the phenomena previously spoken of. For if the sum Σf for the 2s-electrons by the method of § 1 shall be found as much below the value 2 as is shown by table 1, then a considerable fraction (75 per cent or even more) of the atoms originally ionised into L_I by electron-impact must go by the Auger effect into $L_{III} M_{IV}$ or $L_{III} M_V$. But the number of atoms originally ionised into L_I is comparable with that ionised into L_{III} . Hence the intensity of the satellites of the L_{III} -emission lines must be comparable to the intensity of these lines themselves.

We shall go still a step further and try to interpret the peculiar shape of the curve of fig. 1. The probability of an Auger effect in which the electron 1 jumps from a state with wave function $\psi'(1)$ to a state $\psi''(1)$ while the electron 2 jumps from the state $\psi'(2)$ to the state $\psi''(2)$ is proportional to the square of the matrix element ¹⁾

$$v = \int \frac{\rho_1 d\tau_1 \cdot \rho_2 d\tau_2}{r_{12}}, \quad \rho_1 = \psi'(1) \psi''(1), \quad \rho_2 = \psi'(2) \psi''(2),$$

where $d\tau_1$ and $d\tau_2$ are elements of volume, r_{12} their distance. ρ_1 and ρ_2 may be regarded as charge densities due to the two electrons, the electrostatic interaction of which has to be computed. In order to get a strong Auger effect, it is desirable that $\psi'(1)$ and $\psi''(1)$ reinforce each other by suitable overlapping in order to make ρ_1 large, that similarly ρ_2 is also large, and that finally r_{12} is small. As regards this last condition, it is favourable if the electrons 1 and 2 originally are contained in neighbouring shells. In our case $\psi'(1)$ is the wave function $2p$, $\psi''(1)$ the wavefunction $2s$, $\psi'(2)$ the wavefunction $3d$ while $\psi''(2)$ corresponds to the electron ejected with finite kinetic energy W . The angular momentum l'_2 of this ejected electron must have one of the values 1, 2, 3 in units $\hbar/2\pi$. For previous to the Auger effect the two interacting electrons have angular momenta $l'_1 = 1$, $l'_2 = 2$ with vector resultants $L = 1, 2, 3$, while after the Auger effect $l'_1 = 0$ so that $L = l'_2$. From the conservation of L the result mentioned follows directly.

1) G. Wentzel, Zs. f. Phys. **43**, 524, 1927; E. Fues, Zs. f. Phys. **43**, 726, 1927.

In fig. 3 we have shown the approximate size and position of the normalised radial parts P of the various wavefunctions concerned in the atomic number range in which we are interested. r is the distance from the nucleus with the radius of the first B o h r orbit in hydrogen as unit of length. P is really the ordinary radial wavefunction

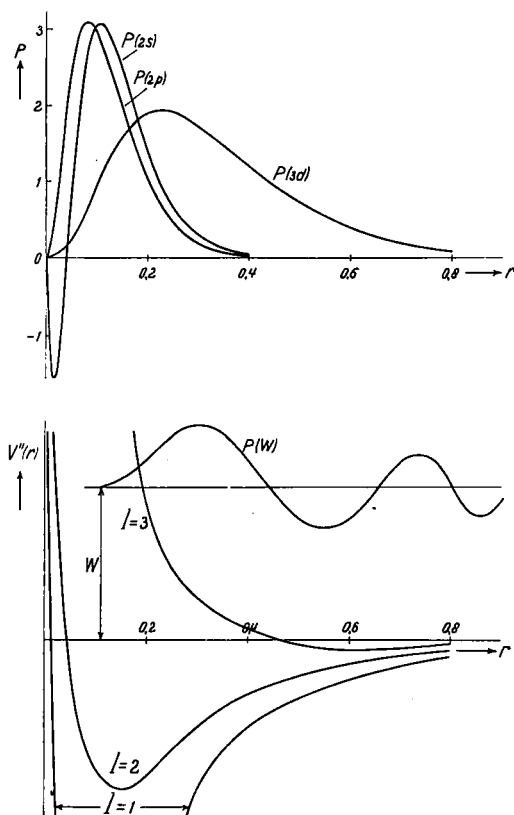


Fig. 3. Radial wavefunctions of the electrons involved in the Auger effect which gives rise to the principal L -satellites. Upper part: Radial wavefunction P of the $2s$ -, $2p$ - and $3d$ -electrons. Lower part: Central fields $V''(r)$ governing the radial motion of an electron with azimuthal quantum number $l = 1, 2$ or 3 . For $l = 3$ and a positive energy W the character of the radial wave function $P(W)$ has also been indicated. The radius r is measured in atomic units. The diagram represents approximately the conditions for elements with atomic numbers near $Z = 50$.

multiplied by r . It is more suitable for our purpose since it is $P^2 dr$ which determines the charge density between concentric spheres of radius r and $r + dr$ for every electron. The functions $P(2p)$ and $P(2s)$ for electron 1 as well as the function $P(3d)$ for electron 2, shown in the upper part of fig. 3, have been taken as those of Cs^+ recently published by H a r t r e e¹⁾. This element, it is true, has an atomic number $Z=55$ somewhat higher than the elements considered, but for a qualitative orientation is suitable enough. It appears that the wavefunctions $P(2p)$ and $P(2s)$ of electron 1 reinforce each other fully in the region where they have their largest numerical values. In order to see how the wavefunction $P(W)$ of the ejected electron overlaps $P(3d)$, we note that $P(W)$ is a solution of the one-dimensional wave equation of an electron moving in the field

$$V''(r) = V(r) + \frac{l_2''(l_2'' + 1)}{2r^2},$$

where $V(r)$ is the H a r t r e e field of the atom. In the lower part of fig. 3 we have drawn this field for $l_2'' = 1, 2, 3$, the three values of l_2'' which according to previous remarks the electron may take after ejection. We have also indicated the wavefunction $P(W)$ for $l_2'' = 3$ and the positive energy of ejection W . As one sees, $P(W)$ for $l_2'' = 1$ and 2 will always be oscillatory in the region where $P(3d)$ is large so that ρ_2 will change sign and keep the integral v small. For $l_2'' = 3$, however, a different behaviour results. If W is small, the first maximum of $P(W)$ lies to the right of $P(3d)$ and there is little overlapping. Consequently v is small. As W increases, the first maximum of $P(W)$ moves to the left till it coincides with that of $P(3d)$. This is the state of affairs shown in fig. 3 which gives rise to a large v . For still larger W the overlapping becomes less perfect, causing v to diminish again. We understand now why, upon decreasing the atomic number below 53, the L_{III} -satellites appear first faintly, then have a maximum and finally decrease again, the energy of ejection $L_I(Z) - L_{III}(Z) - M_{IV,v}(Z + 1)$ increasing slowly from zero for $Z = 53$ to larger values as Z becomes less (see fig. 2). The whole consideration is really nothing else than an application of the F r a n c k - C o n d o n principle to the ejected electron. The chance of ejection will be particularly great if after the energy transfer the electron 2

1) D. R. H a r t r e e, Proc. Roy. Soc. **143**, 506, 1934.

has such an energy W and angular momentum l_2'' that its motion has a point of reversal at the value of r where before the radiationless transition the electron by preference is found (maximum of $P(3d)$).

Two other facts concerning the satellites in the L -series may finally be mentioned here as they are also in accord with the view-point proposed. The first is the much greater weakness and the absence of any intensity anomaly for the satellites of $L\beta_1$ (transition $L_{II} \rightarrow M_{IV}$)¹⁾, corresponding to the fact that the energy difference $L_I - L_{II}$ for $Z > 40$ is not sufficient to eject an M -electron. The second is the behaviour of the satellites of $L\alpha$ and $L\beta_2$, discussed above, in the case of fluorescent excitation. While the intensity of the K -satellites relative to the parent lines is found to be much greater with cathode ray excitation than with fluorescent excitation²⁾, new measurements of Hirsch and Richtmyer³⁾ yield identical intensity ratios for these L -satellites if care is taken that the incident radiation not only can excite L_{III} but also L_I (line excitation with $h\nu$ greater than L_I). Indeed, if the satellites are primarily due to the reorganisation of the atom on account of the Auger effect $L_I \rightarrow L_{III}$ and not to direct double excitation, their intensity relative to the L_{III} -lines will remain unchanged as long as the number of atoms ionised into L_I stays the same in comparison to those ionised into L_{III} , the mode of excitation being quite indifferent.

§ 3. *Broadening of the X-Ray Emission Lines.* The Auger Effect $L_I \rightarrow L_{III}$ and the analogous Auger effects in the M -, N -, . . . shells are also responsible for a phenomenon to which Coster⁴⁾ has drawn attention already some time ago. It appears that there is a noticeable difference in the sharpness of the X -ray levels differing only by the quantum number l , large values of l being favourable to greater sharpness. Thus L_{II} and L_{III} with $l = 1$ seem sharper than L_I with $l = 0$, and quite analogous remarks apply to the M -levels. New quantitative determinations by Richtmyer, Barnes and Ramberg⁵⁾ entirely confirm this conclusion. This is just what one might expect, the life time of the state L_I being

1) D. Coster, Phil. Mag. **43**, 1070, 1922; see p. 1089.

2) D. Coster and M. J. Druyvesteyn, Zs. f. Phys. **40**, 765, 1927.

3) F. R. Hirsch and F. K. Richtmyer, Phys. Rev. **44**, 955, 1933.

4) D. Coster, ZS. f. Phys. **45**, 797, 1927.

5) F. K. Richtmyer, S. W. Barnes and E. Ramberg, Phys. Rev. **46**, 843, 1934.

reduced with respect to that of L_{II} and L_{III} by the radiationless transition in question.

More particularly it becomes intelligible on the basis of the preceding discussion why the L -emission lines of the elements La ($Z = 57$) and the rare earths following it are in general sharper than those of the elements with Z between 40 and 50, a fact to which attention had also been drawn ¹⁾.

Our considerations lead to some additional conclusions which are capable of experimental verification. In the first place the deficit in intensity of the L_I -emission lines relative to the L_{II} - and L_{III} -emission lines for the elements between $Z = 53$ and $Z = 74$ should be much less pronounced than for Ag , Pt and Au . In the second place the minimum energy for excitation of the L_{III} -satellites with fair intensity should not be $L_{III} + M_{VI, V}$ but L_I . Finally the existence of the slow Auger electrons due to the radiationless transition $L_I \rightarrow L_{III}$ should be capable of verification. Investigations are in progress in this laboratory to test these conclusions.

November 26th, 1934.

1) D. Coster, Phil. Mag. **44**, 546, 1922; see p. 548.