Since it has been definitely shown in this and other investigations that the final levels in absorption edge transitions are lattice levels, and since the l selection rule is evidently giving the preferred transitions in many cases, it may be concluded that the M discrepancies arise because the M and L electrons may not all go the same level. One should expect, as has so far often been the case, M_1, M_4, and M_5 discrepancies but none for the M_2 and M_3 edges.[50]

For helpful assistance and counsel I wish to express my thanks to the staff of the Department of Physics of the State University of Iowa and especially to Professor G. W. Stewart who suggested the problem and directed the research.

[50] If computations are made on the basis of the observed L_3 edge energy.

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New X-Ray Lines in the L Series Resulting from K Auger Transitions

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Three new x-ray lines in the L series of silver were found which have wave-lengths of 4.030A, 4.016A, and 3.805A. A fourth and much fainter line was found at 4.023A. These lines are due to processes in which an atom, initially ionized in the K shell, undergoes transitions of the type

$K \rightarrow LL +$ expelled electron (Auger transition)
$LL \rightarrow LM +$ quantum (radiative transition).

These lines differ from those previously observed from multiply ionized atoms in that they are more widely separated both from each other and from the diagram lines. An x-ray vacuum spectrograph capable of withstanding a potential of 100 kv across the x-ray tube was used in the observation of these lines. The anode of the x-ray tube was a thin foil of silver backed with aluminum. Special precautions were necessary to suppress the continuous background radiation in the region of the lines as the expected intensity of the lines was of the same order of magnitude as the intensity of the diagram line arising from the transition L_{III} to N_{I}.

Introduction

THIS paper presents the result of a search for some faint lines predicted in the L spectrum of silver.

A great deal of effort has been expended in the search for nondiagram lines in various atoms in an effort to learn more about atomic structure. Nondiagram lines were first observed by Siegbahn and Stenstrom[1] while they were studying the K series of the elements Na(11) to Zn(30), and have been reported by numerous others[2] a few of whom are listed in this paper.

Multiple ionization of the atom was assumed to explain the presence of these lines. Some of the early theories assumed that the atom was multiply ionized by a single electron impact while others assumed that the multiple ionization was due to successive ionizations by different impacting electrons. These theories were mainly at fault in that the predicted intensities were not in agreement with the experimentally observed intensities. Some of the theories attributed the lines to single transitions in multiply ionized atoms while others attributed them to double transitions in multiply ionized atoms.

Coster and Kronig[3] have improved the theory to account for the intensity of the L satellites by assuming an Auger[4] transition from L_{I} ionization to L_{III} with an accompanying M_{IV} or M_{V} ionization. This leaves the atom doubly ionized, which is the initial condition for the production of satellites. The number of atoms originally ionized in L_{I} is comparable to the number ionized in L_{III}

[1] Siegbahn and Stenstrom, Physik. Zeits. **17**, 48 (1916); **17**, 318 (1916).
[2] G. Wentzel, Ann. d. Physik **66**, 437 (1921). D. Coster, Phil. Mag. **43**, 1070 (1922). A. Larsson and M. Siegbahn, Ark. f. Mat. Astron och Fysik, Stockholm **18**, 18 (1924). G. Wentzel, Zeits. f. Physik **31**, 445 (1925). L. A. Turner, Phys. Rev. **26**, 143 (1925). T. Wetterblad, Zeits. f. Physik **43**, 767 (1927). M. J. Druyvesteyn, Dissertation, Groningen (1928).
[3] D. Coster and R. de L. Kronig, Physica **2**, 13 (1935).
[4] P. Auger, J. de phys. et rad. **6**, 205 (1925).

so the intensities of L_{III} satellites will be comparable to the intensities of the parent lines. This is upheld by experiment.

Coster and Kronig compared the energy difference $WL_I - WL_{III}$ of any element Z with the energy WM_{IV} or WM_V of element $Z+1$ as a function of the atomic number. They showed that in the region where the $L\alpha$ and $L\beta_2$ satellites are absent $WL_I - WL_{III}$ is smaller than WM_{IV} or WM_V. Thus they conclude that these satellites must be almost exclusively due to the Auger effect.

While studying information concerning the production of satellites, D. L. Webster observed that there should be another set of faint lines much farther from the diagram lines than those previously found. The double ionization in the L shell may be produced in a different way. An atom ionized in the K shell, filling the vacancy from the L shell, may either emit a photon corresponding to one of the $K\alpha$ lines or it may, by an Auger rearrangement, emit a photoelectron from the L shell, thereby leaving the atom with a double ionization in the L shell. Secondary photoelectrons have been found with energies equal to the difference between the energy of the $K\alpha_1$ line and the energy of an L limit; therefore such photoelectrons must leave double L ionizations. These atoms are in the proper state to emit these new faint lines.

To get double ionization in the L shell by this method, the atom must first be ionized in the K shell. These faint lines, due to double L ionization, should appear only when the energy of the electrons in the cathode stream is in excess of the K excitation energy of the atom in question.

Theory

The theory given here is used to estimate the probable intensity of these faint lines and to calculate the locations of these lines with sufficient accuracy to allow intelligent search for them.

The ratio of the intensity to be expected of these satellites to the intensity of the line resulting from an analogous transition in a singly ionized atom will depend upon: (1) the ratio of the number of Auger transitions in which an L electron is emitted to the number of K ionizations; (2) the ratio of the number of K ionizations to the number of L ionizations which may result in the normal line. Without rigorous calculation Wentzel[5] has shown that the lifetime of the K state, with respect to an Auger transition in which an L electron is emitted, is of the order of 10^{-15} second. The effective lifetime for radiation of x-rays of 0.56A (the wave-length of Ag K) is 2.6×10^{-16} second. For silver, therefore, about one-fourth of the K series quanta result in the Auger emission of an L electron. This agrees with the work of Balderston[6] who has made measurements of the fluorescence yield from radiators of Fe(26), Ni(28), Cu(29), Zn(30), Mo(42), and Ag(47). His value for the fluorescence yield of Ag(47) is 0.75.

To obtain a rough estimate of the ratio of the number of K ionizations to the number of L ionizations which may result in the normal line we may use the ionization function of Rosseland.[7] This function gives the number of ionizations in shells having an ionization energy E_q per unit path length of a β-ray moving at uniform speed through the target material.

$$\Phi(E, E_q, n_q) = (n_q e^4/E)(1/E - 1/E_q).$$

E is the energy of the impacting β-ray, E_q is the energy required to remove an electron from the shell ionized, n_q is the number of electrons per unit volume having a binding energy E_q, e is the electronic charge. By use of this function, the ratio of the numbers of ionizations in the K and the L_{III} shells is found to be 0.012 for electrons impinging at 40 kv.

Combining these two results, we should expect the sum of the intensities of the lines resulting from transitions into doubly ionized L_{III} shells to be 0.3 percent of the intensity of the normal L lines. This is about the same as the intensity of the diagram line arising from the transition L_{III} to N_I.

All wave-length calculations will be applied to the transition double L_{III} ionization to L_{III} and M_V ionization. The results of the calculations applied to other transitions will be given later in a table. Four different methods of estimating the wave-length of the line due to the above transition will be outlined in this section.

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[5] G. Wentzel, Zeits. f. Physik **43**, 524 (1927).
[6] M. Balderston, Phys. Rev. **27**, 696 (1923).
[7] S. Rosseland, Phil. Mag. **45**, 65 (1923).

These lines should be singlets and triplets as they arise from a transition into a doubly ionized shell. The normal L diagram lines arise from a transition into a singly ionized shell and therefore are doublets.

The calculations to follow are only rough approximations as the coupling between the electrons will not be considered.

For the first method we use as an approximation to the energy of the initial state twice the ionization energy of an L_{III} electron plus the energy W_H needed to extract an electron from a hydrogen atom starting from a distance r equal to the radius of the L_{III} shell of the atom in question. An approximation to the energy of the final state is the extraction energy of an L_{III} electron of the atom in question plus the extraction energy of an M_V electron of the element whose atomic number is greater by one than that of the atom in question.

Combining, we have an expression for the energy of the line, for silver,

$$W_{AgL_{III}}+W_H-W_{CdM_V}.$$

Substituting numerical values in the equation and changing energies to angstrom units we get a wave-length of 3.94A.

A second way to estimate the position of the line is to extract the second L_{III} electron in two steps. First move it as far as the M_V shell. For Ag the energy required for this is equal to the energy of $AgL\alpha_1$, plus some fraction of the difference between this energy and that of $CdL\alpha_1$. This fraction is the average of the screening factor of one L electron on another in the same shell, 0.35, and the screening factor of an L electron on an electron in the next shell farther out, 1.0. This average is 0.675. Now take the electron the rest of the way out of the atom. The energy required to do this is just a little less than the energy of the M_V limit of In(49) and will be called $(W_{InM_V})^*$. After the transition, the energy of the atom is equal to $W_{AgL_{III}}+W_{CdM_V}$. The energy of the satellite is then given by the expression,

$$W_{AgL}+0.675(W_{CdL}-W_{AgL})+(W_{InM_V})^*-W_{CdM_V}.$$

By substitution of numerical values in this expression, the energy of the line is found to be 3.14 kilovolt-electrons which corresponds to 3.94A wave-length.

The third line of attack also starts by extracting one L_{III} electron whose extraction energy is given by the normal L_{III} limit. For the second L_{III} electron, the energy required to extract it will be assumed to be greater than that required for the previous one by an amount equal to 0.675 of the difference in energy between CdL_{III} and AgL_{III}. The energy of the line is

$$W_{AgL_{III}}+0.675(W_{CdL_{III}}-W_{AgL_{III}})-W_{CdM_V}.$$

By substitution of the numerical values in this expression we have 3.11 kv or 3.98A for the wave-length of the line.

The fourth method is to use Slater's[8] screening constants throughout to calculate the energy difference between the two states of the atom. By this method the difference between these two energies is 3240 electron volts, which corresponds to 3.81A.

Apparatus

The apparatus does not differ from the conventional vacuum spectrograph except in two respects. The x-ray tube should be able to withstand a potential of 100 kv and should have a special anode which will be described presently.

The difficulties encountered in recording these faint lines on a photographic film are not due solely to their low intensity, as this could be overcome by a longer exposure time, but are also due to the masking effect of the background. The high voltage necessary for the production of the new lines increases the continuous background over that produced by the low voltage usually used to photograph this wave-length. It does this in two ways: first, the intensity of the continuous radiation in the vicinity of the lines is increased; and second, the continuous radiation of shorter wave-lengths is greatly increased. This radiation increases the background in the vicinity of the lines by higher order reflection from the crystal. The intensities to be expected of the lines would not be sufficient to make them observable above the background of continuous radiation from a thick target, but with proper care taken to suppress the background the lines become evident.

[8] J. C. Slater, Phys. Rev. **36**, 57 (1930).

As the voltages used in this research are from 6 to 30 times the voltage necessary to produce 4A radiation, there might be from 6 to 30 higher orders present and it was found that with ordinary solid targets the film was completely blackened long before any new line was visible at all.

A thin target was used as a means of suppressing the continuous radiation.

Consider the target as divided in two parts: a thin surface layer of thickness sufficient to practically absorb 4A x-rays, and the remainder of the target. Then all the rays we are interested in must necessarily come from the surface layer; the remainder of the target contributes nothing. Moreover, this backing is actually a detriment, for the cathode rays after passing through the front layer have sufficient energy to produce continuous rays of shorter wave-lengths, which penetrate the surface layer and produce high order continuous background. Also, some of the cathode rays that enter the back section of the target get turned around (rediffuse) and retraverse the front layer, where they may produce continuous quanta but are not likely to produce the desired ionizations, because by the time they have rediffused most of them have lost too much energy.

Thus, for the some number of cathode rays, the thin layer alone is much more effective for our purpose than the whole target and we would be tempted to try an unbacked thin target. But there are enormous difficulties in getting rid of the heat generated and the result is that unbacked targets have to be run on very small powers. The correspondingly enormous exposure times needed for faint lines render unbacked targets impractical for our purposes.

The next best thing is to use a thin target backed with some material that will remove the heat but will give the least possible continuous radiation and rediffusion. Both these are increasing functions of the atomic number, so we choose the element of the lowest atomic number contingent on its also having good heat conductivity and reasonable mechanical properties. Aluminum seems best.

TABLE I. *Calculated wave-lengths.*

Transition	Method of Calculation 1	2	3	4	Average
$L^2{}_{III}-L_{III}M_V$	3.94A	3.94A	3.98A	3.81A	3.918A
$L^2{}_{II}-L_{II}M_{IV}$	3.94A	3.75A	3.82A	3.81A	3.830A
$L^2{}_{III}-L_{III}N_V$	3.83A	3.40A	3.57A	3.27A	3.417A

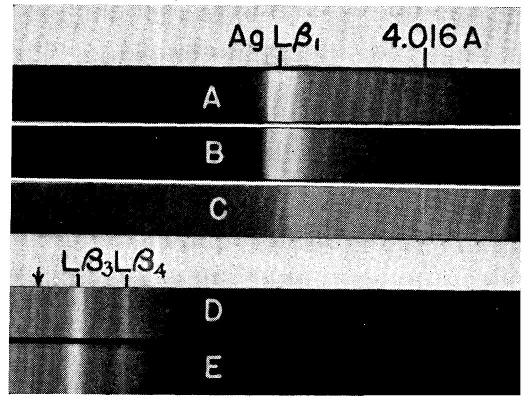

FIG. 1. X-ray spectrograms showing the new lines. A, 80 kv, 2.5 ma, 10 hours exposure. B, 20 kv, 10 ma, 2.5 hours exposure. C, 80 kv, 5 ma, 10 hours exposure. D, 80 kv, 5 ma, 10 hours exposure. E, 20 kv, 10 ma, 5 hours exposure.

Silver was chosen as the target material for several reasons. Silver is easy to get in a thin film by evaporation in a vacuum. Further, extensive measurements have been made on the spectrum of silver with respect to the fluorescence efficiency and the relative intensities of the lines in its spectrum. The lines that we are looking for would fall in the range where we could use a calcite crystal.

Provision must also be made to exclude visible radiation from the photographic film.

A cassette was used which would allow four pictures to be taken at one loading so there would not be any differences introduced in the pictures in the developing process.

RESULTS

Three new lines were found to be present on the films taken above the K excitation potential and were not present on the films when the tube was run at lower potentials. On measurement, the wave-lengths were found to be 4.030A, 4.016A and 3.805A.

The films from which these measurements were taken are shown in Fig. 1.

The spectrum shown in Fig. 1A was taken at 80 kv, 2.5 ma with 10 hours exposure. Fig. 1B was taken at 20 kv, 10 ma, with 2.5 hours exposure. The faint lines are clearly visible in A but not in B.

Figure 1C shows an exposure at 80 kv, 5 ma, 10 hours which is double the previous exposure. The lines are more in evidence.

The spectrum shown in Fig. 1D was taken at 80 kv, 5 ma, 10 hours and Fig. 1E at 20 kv, 10 ma and 5 hours exposure. A faint line is present in D at the point marked with the arrow but is absent in E.

These measured wave-lengths are to be compared with the various estimated wave-lengths which are given in Table I.

The agreement is as good as can be expected when one considers the approximations made in estimating the wave-lengths.

A subsequent paper by Richtmyer[9] shows that the transitions indicated above should be

$$L_{\mathrm{II}}L_{\mathrm{III}}(2)\rightarrow L_{\mathrm{III}}M_{\mathrm{IV,\,V}}$$
$$L_{\mathrm{II}}L_{\mathrm{III}}(2)\rightarrow L_{\mathrm{II}}M_{\mathrm{IV,\,V}}$$
$$L^2_{\mathrm{III}}(2)\rightarrow L_{\mathrm{III}}M_{\mathrm{IV,\,V}}.$$

A faint line was noticed between the two lines 4.030A and 4.016A but was not reported in the author's Ph.D. thesis because it was so faint and because of the desire to be certain of those lines reported. This line, however, seems to receive some verification in the calculations by Richtmyer.

Further evidence that the mechanism of production of these lines is understood comes from the intensities. These were determined by calculation from two quantities. One of these was the ratio of the intensities of the new faint lines which were calculated by the method given in the section on the theory of the intensities of these faint lines. The other quantity used was the length of time known experimentally to give a satisfactory density of the diagram lines on the film. It can be seen from the prints of the films, which were exposed for the calculated duration of time, that the new lines are clearly evident. Therefore the observed intensities are in rough agreement with the calculated values.

Finally the fact that these lines appear only above the K excitation potential shows that they must involve a K ionization as was assumed. On the other hand all previous L satellites have appeared at voltages only slightly in excess of the L ionization potential.

It is therefore concluded that the lines found were due to a double ionization in the atom caused by an Auger transition.

[9] R. D. Richtmyer, Phys. Rev. 56, 146 (1939).

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Theory of the X-Ray Lines *LL–LM*

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The quantum theory is applied to the calculation of the x-ray line structure to be expected from transitions, between doubly-ionized states, of type LL to LM (we indicate missing electrons). Energy levels and wave-lengths are calculated for the silver atom according to usual ideas of atomic structure. For the calculation of the relative intensities it is assumed that the excitations of the initial (LL) levels arise from internal conversion of K excitation energy. The predicted structure agrees quite satisfactorily with the structure observed by C. J. Burbank and described in the preceding paper.

I. Introduction

The preceding paper[1] by Burbank describes some faint lines in the x-ray spectrum of silver and shows that they are due to processes in which an atom, initially ionized in the K shell, undergoes transitions of the type

$$K\rightarrow LL+\text{expelled electron} \quad \text{(Auger transition)}, \quad (1)$$

$$LL\rightarrow LM+\text{quantum} \quad \text{(radiative transition)}. \quad (2)$$

[1] C. J. Burbank, Phys. Rev. 56, 142 (1939).

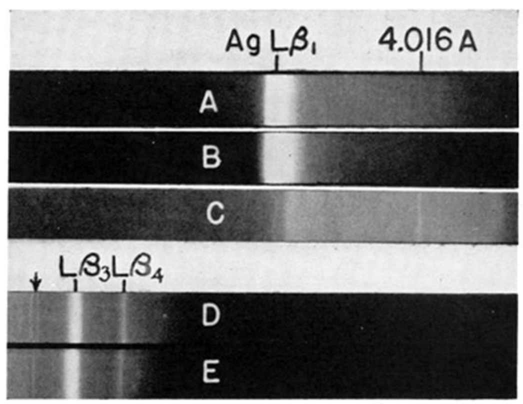

FIG. 1. X-ray spectrograms showing the new lines. A, 80 kv, 2.5 ma, 10 hours exposure. B, 20 kv, 10 ma, 2.5 hours exposure. C, 80 kv, 5 ma, 10 hours exposure. D, 80 kv, 5 ma, 10 hours exposure. E, 20 kv, 10 ma, 5 hours exposure.