Excitation Potential, Relative Intensities and Wave-Lengths of the $K\alpha''$ X-Ray Satellite Line

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With a two-crystal vacuum spectrometer, ionization curves of the $K\alpha''$ satellite line have been recorded for elements S(16) to V(23). This satellite line, on the short wave-length side of and very close to the $K\alpha_1$ line, was observed in 1922 by Dolejšek and has been until now a forgotten line. The excitation potential of this satellite has been determined: The initial atomic state for its emission appears to be one of KM ionization. The $K\alpha''$ intensity relative to the $K\alpha_1$ intensity varies with atomic number, reaching a maximum of 2.3 percent at Ca(20). The $K\alpha''$ wave-length positions have also been determined for each element. The observed data are compatible with both the Wentzel-Druyvesteyn and the Richtmyer theories for the origin of this satellite line.

I. INTRODUCTION

SATELLITES comprise a large fraction of the total number of characteristic x-ray emission lines; but as yet we do not have a generally acceptable explanation of satellite origins. The greatest need in resolving this enigma is that of a more complete and accurate experimental description of these nondiagram lines.

In another paper[1] the writer has recently reported the results of experiments on the excitation potential of the satellite lines of the $K\alpha_{3,4}$ group. This group of lines consists (for elements near titanium ($Z=22$)) of five components: α', α_3, α_3', α_3'' and α_4. For these lines[2] the excitation potential was found to be in agreement with the voltage required to ionize doubly the emitting atom by ejection of a K and an L electron by a single cathode-ray impact. This result is in support of the Wentzel-Druyvesteyn theory which supposes that the atomic (or ionic) transition $KL\rightarrow LL$ gives rise to the $K\alpha_{3,4}$ lines. The present paper is concerned with determinations of the excitation potential, relative intensities and wave-lengths of the $K\alpha''$ satellite line. We shall conclude that this line is not of the $\alpha_{3,4}$ group but, in terms of the Wentzel-Druyvesteyn theory, is produced by a $KM\rightarrow LM$ transition.

II. EXPERIMENTAL PART

The two-crystal vacuum spectrometer, on which were mounted calcite crystals A_1B_4, was used in the present as in the previous experiments.[1] The advantages of this type of instrument over the single-crystal spectrograph are (1) in the greater practical resolving power and dispersion, and (2) in the greater accuracy with which intensities can be measured. The relative disadvantages of the ionization method of registering intensities as compared with the photographic method are (1) in the greater difficulties encountered in preparing satisfactory targets of the materials to be studied, and (2) in maintaining the higher vacuum in the x-ray tube necessary for accurate intensity measurements. These advantages and disadvantages have been mentioned elsewhere.[1,3] The reader is referred to previous papers for discussions of the accuracy[1] with which the present ionization curves[4] were recorded and of the instrument perturbations[5] which distort the true x-ray line contours into the observed curves.

The targets used in these experiments were prepared as follows: $CaCl_2$, KCl, $SrCl_2$, K_2PO_4, CaO and Sc_2O_3 in the powdered form were pounded into a roughened copper surface. CuCl was formed by passing chlorine gas over copper. A metallic calcium target was made in the manner previously described.[6] The pure metallic titanium and vanadium targets have also been

* The author is indebted to the Carnegie Foundation for a grant-in-aid of this research.

[1] L. G. Parratt, Phys. Rev. **49**, 132 (1936).

[2] The intensity of the two strongest lines, α_3 and α_4, dominates the intensity of the group, and, as discussed in reference 1, whether or not all five components of the group have the same excitation potential could not be determined in these experiments.

[3] L. G. Parratt, Rev. Sci. Inst. **6**, 372 (1935).

[4] The experimental set-up in the present work was identical with that in the previous work, reference 1.

[5] L. G. Parratt, Rev. Sci. Inst. **6**, 387 (1935).

[6] L. G. Parratt, Phys. Rev. **44**, 695 (1933).

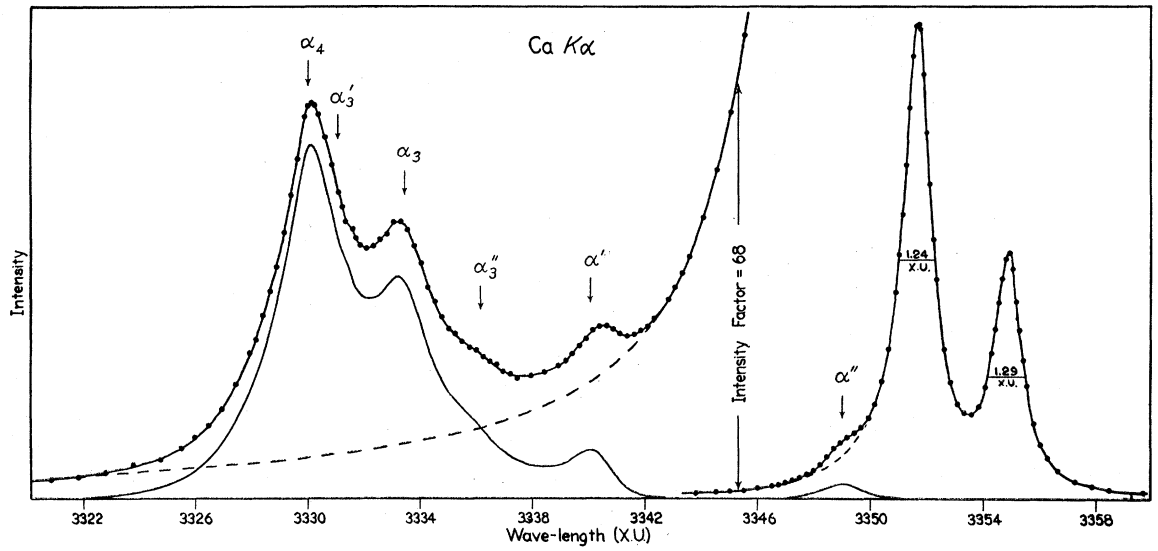

FIG. 1. Ionization curve of the Ca $K\alpha$ region. This curve was recorded with a CaO target and with a tube potential of 20 kv. The $\alpha_{3,4}$ group of satellites is plotted to an intensity scale 68 times the scale used in plotting the α'', α_1 and α_2 lines. The satellite background (the side of the α_1 line) has been sketched in and the satellite contours, corrected for this background, are also drawn in the figure.

described,[3,6] and likewise the sulphur targets.[7] All of these targets were satisfactory in studying the $K\alpha_{1,2}$ doublet and the $K\alpha''$ lines, but only FeS, K_2PO_4, CaO, Sc_2O_3, questionably $CaCl_2$, and metallic Ca, Ti and V served satisfactorily in obtaining data on the $K\alpha_{3,4}$ lines. This latter group of targets would dissipate, with the focal spot approximately 2 mm in diameter, from 400 to 700 watts of power.

Notation

The term $K\alpha''$ in the present paper is used to refer to the "bump" which appears on the short wave-length side, near the base, of the $K\alpha_1$ line with elements S(16) to V(23). That the reader may gain perspective, an ionization curve of the $K\alpha$ region, $K\alpha_{1,2}$, α'' and the $\alpha_{3,4}$ group, for calcium (20) is shown in Fig. 1. Ca $K\alpha''$ appears at the wave-length 3349.1 X. U. In Fig. 1 of the previous paper[1] the same $K\alpha$ region is reproduced for titanium (22).

The notation used to designate x-ray satellites is confused; this confusion becomes more apparent as our knowledge of these lines becomes more complete. Many faint x-ray lines known in the literature as satellite or nondiagram lines can now be accounted for easily as diagram lines for which the quadrupole, rather than the dipole, selection rules are obeyed. Another type of confusion is illustrated by the following: Hulubei recently reported[8] a triplet nature of the $K\alpha_{3,4}$ satellites in the region of elements Cu(29) to As(33). The third component of this group, the one between α_3 and α_4, Hulubei calls α_3'. This is an extrapolation of the notation of Bäcklin[9,10] from the range of elements Si(14) to Cl(17). The writer, using the two-crystal spectrometer, has been able to trace[11] the component α_3' from S(16) to Ge(32). Relative to the α_3 or to the α_4 line, α_3' moves progressively as the atomic number changes: In the region of low atomic numbers the α_3' is in the position reported by Bäcklin[9] and by Ford,[10] that is, on the *long*[12] wave-length side of

[7] L. G. Parratt, Phys. Rev. **49**, 14 (1936).

[8] M. H. Hulubei, Comptes rendus **201**, 544 (1935).

[9] E. Bäcklin, Zeits. f. Physik **33**, 547 (1925); **38**, 215 (1926).

[10] O. R. Ford, Phys. Rev. **41**, 577 (1932).

[11] Discussed in more detail in another paper in process of publication.

[12] If these trends are extrapolated to atomic numbers lower than Si(14) the α_3 and α_3' lines should be coincident in wave-length at Al(13) or Mg(12): In fact, with these elements, Al and Mg, no α_3' has been found while the relative intensity of α_3 has been reported as being anomalously large (reference 10). From ionization curves at S(16) the writer estimates the intensity of the resolved α_3' component to be approximately 80 percent of the intensity of the α_3 component. With elements of atomic number less than 12 the α_3' line may be expected to appear, if one continues the extrapolation, on the long wave-length side of α_3.

α_4; at Ti(22) the α_3' and α_4 are coincident in wave-length; and with elements of atomic number greater than 22 α_3' is on the *short* wave-length side of α_4. These observations, in agreement with those of Hulubei, show that in the range of higher atomic numbers $\alpha_{3,4}$ is complex, actually a quadruplet since the α' line, although very faint, is still present, and also show that the terms α_3' and α_4 as assigned by Hulubei should be interchanged.

A third type of confusion in notation is in regards to the present line $K\alpha''$. In 1922 Dolejšek[13] observed an "emission band" on the short wave-length side of the $K\alpha_1$ line with elements Cl, K, Ca and Sc. The short wave-length edge of this band he called α'; the line now known as α' Dolejšek, following Siegbahn's lead, called α_7. Dolejšek's "emission band" and the writer's "bump," α'', are the same line (or group of lines). It speaks well of Dolejšek's care in his observations and of the resolving-power of his spectrograph that he was able to detect this emission band: Of the numerous investigators following him, none, so far as the writer is aware, has reported finding it.

Druyvesteyn[14] refers to Dolejšek's emission edge α' as the α'' line, and reverts to Hjalmar's[15] use of the term α'. In Fig. 1 the α' line is at 3340.1 X. U. Deodhar[16] has reported a possible doublet nature of the $K\alpha'$ line with elements Si(14) and P(15). The terms α' and α'' were used by Deodhar to refer to this doublet. So far as the writer is aware no other observer has seen a doublet structure in α' for Si, P or other elements, and the writer has found no indication of such structure for S(16). Deodhar states that his α'' may have been due to chemical combination or may have been spurious. We shall therefore adhere to the notation used by Druyvesteyn in assigning the term α'' to the "bump."

Relative intensities

Ionization curves of $K\alpha''$ with elements S(16) to Cr(24) are reproduced in Fig. 2. The α'' line is most prominent at Ca(20). This may or may not mean that the intensity of α'' relative to the intensity of α_1 is a maximum at Ca: We do not know the shape of the α_1 line and consequently we have considerable latitude in drawing in the background of the α'' satellite. In Fig. 2 the side of the α_1 line for each element has been drawn in such that the width at half-maximum intensity of the α'' line is approximately the same as the width of the α_1 line. There is no justification for choosing this particular resolution; in fact, satellite lines in general are wider than the associated diagram lines: The component lines of the Ca $K\alpha_{3,4}$ satellites are 1.5 to 3 times as wide as the α_1 line. Furthermore if α'' is in reality a group of lines the width should certainly be greater than is here assumed. This question bears not only on the shape and possible multiplet structure of α'' but also on the asymmetry of the α_1 lines, a subject beyond the scope of the present paper.[11] In Fig. 3 is plotted the intensity of α'' relative to the intensity of α_1 when the resolution is arbitrarily made as indicated in Fig. 2. These intensity ratios are listed in Table I. The uncertainty in the relative intensity due to the indefinite background is greatest for S(16) and, with this element, may be as great as a factor of two or even three. The values given in Table I are probably a minimum. A slight trace of the existence of α'' for Cr(24) was observed but this evidence was within the observational error. The reality of the presence of α'' for V(23) may be questioned since the "bump" with this element is close to the observational error.

TABLE I. *Relative intensities and wave-lengths of the $K\alpha''$ satellite line.* Four different chemical compounds of Cl(17), $CaCl_2$, KCl, CuCl and $SrCl_2$, and two chemical compounds of Ca(20), $CaCl_2$ and CaO, in addition to metallic Ca were used as targets. No difference in the α'' line due to chemical binding was observed greater than the observational error. In the case of CaO and metallic Ca, however, a marked difference is observed in the widths of the $\alpha_{1,2}$ lines. See Figs. 1 and 4. The wave-lengths given by Dolejšek[13] for the short wave-length edge of his "emission band" are listed in the last column. Dolejšek did not give wave-lengths of the $K\alpha_1$ line.

Target	Element	Relative Intensity $(\alpha''/\alpha_1)\times 100$	Wave-Lengths α_1*	α''	α'' (Dolejšek)
FeS	S(16)	1.0	5361.28	5358.6	——
$CaCl_2$	Cl(17)	1.4	4718.2	4714.8	4712
K_2PO_4	K(19)	2.1	3733.68	3730.9	3730
CaO	Ca(20)	2.25	3351.69	3349.1	3349
Sc_2O_3	Sc(21)	1.4	3025.03	3022.8	3023
metal	Ti(22)	0.9	2742.87	2740.9	——
metal	V(23)	0.3	2498.42	2496.5	——

* The wave-lengths of the $K\alpha_1$ line of vanadium and of titanium are taken from Bearden and Shaw, Phys. Rev. **48**, 18 (1935); of scandium to chlorine from Siegbahn, *Spektroskopie der Röntgenstrahlen* (1931); and of sulphur from Valasek, Phys. Rev. **43**, 612 (1933).

[13] M. V. Dolejšek, Comptes rendus **174**, 441 (1922).
[14] M. J. Druyvesteyn, Doctor's Dissertation, Groningen, 1928.
[15] E. Hjalmar, Zeits. f. Physik **1**, 439 (1920).
[16] G. B. Deodhar, Proc. Roy. Soc. **A131**, 633 (1931).

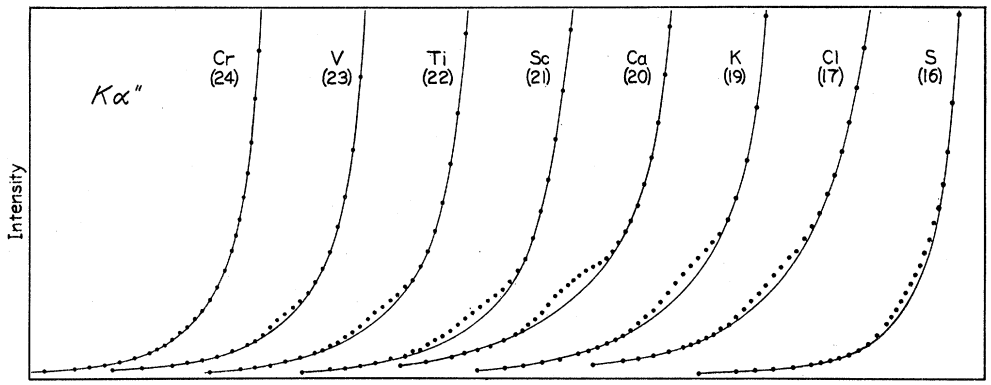

FIG. 2. Ionization curves of the $K\alpha''$ line for elements S(16) to Cr(24). The tube potential used in recording these curves was 15 to 20 kv. The abscissae and ordinate scales are arbitrary in the case of each curve.

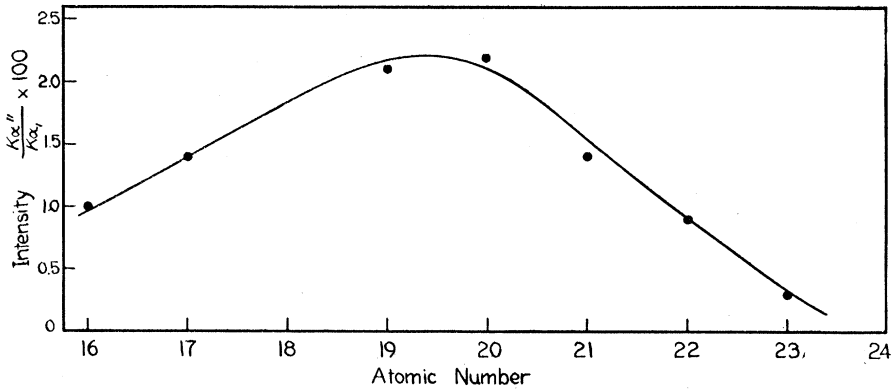

FIG. 3. Intensity of the $K\alpha''$ satellite line relative to the intensity of the $K\alpha_1$ line for elements S(16) to Cr(24). As mentioned in the text, these values are very sensitive to slight changes in the arbitrarily assumed shapes of the α_1 lines: Whether or not this curve reaches a maximum point depends upon the shape one chooses to draw in each of the curves of Fig. 2.

Wave-lengths

Measured from the peak of the $K\alpha_1$ line as a standard, the wave-length positions of the peaks of the α'' lines, resolved as discussed above, are as given in Table I. Only differences in wave-length can be accurately measured with the writer's spectrometer, so the wave-lengths of the α_1 lines used as references are included in the table. Surprisingly good agreement exists between the present α'' wave-lengths and those given by Dolejšek for the edge of his "emission band."

Excitation potential

As discussed in the previous paper[1] a knowledge of the minimum voltage required to produce a given satellite line is especially requisite in developing or in testing any theory of satellite origin. In the case of the $K\alpha''$ satellite, however, the two principal contemporary theories, the Wentzel-Druyvesteyn theory[14] and Richtmyer's "double-jump" theory,[17] predict the same excitation potential: The initial state of the atom emitting the $K\alpha''$ line is supposed in each case to be that of KM ionization.

Fig. 4 shows ionization curves of Ca $K\alpha''$ recorded at various voltages. For these curves a consistency in the background is managed by superimposing the observed curves, matched in intensity at the α_1 peak, on an assumed but *fixed* α_1 shape. Consequently, the differences in the relative intensity which may be present with

[17] F. K. Richtmyer, J. Frank. Inst. **208**, 325 (1929).

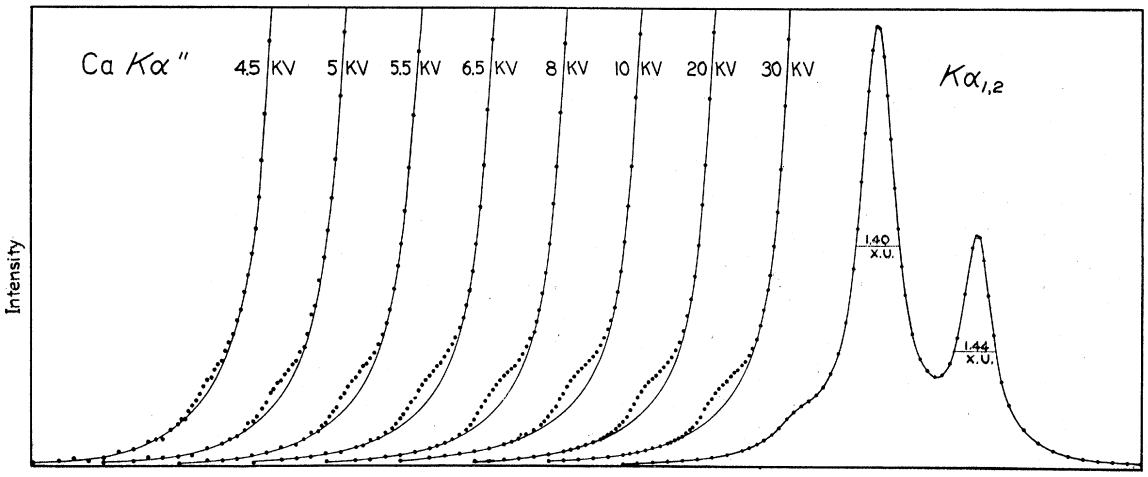

FIG. 4. Ionization curves of Ca $K\alpha''$ recorded at various tube voltages. A metallic calcium target was used. No *relative* uncertainty is present in the background of these curves as discussed in the text.

Although there is a very pronounced difference in the widths of the Ca $K\alpha_{1,2}$ lines observed from targets of metallic calcium and of CaO (Fig. 1), no difference in the α'' satellite was observed greater than the observational error.

different tube voltages or tube currents can be measured without the background uncertainty mentioned above. In testing for a possible effect of chemical binding by using targets of calcium oxide and of metallic calcium the background uncertainty is again large because of the different α_1 shapes. See the widths of α_1 in Figs. 1 and 4.

The α'' relative intensity was observed to be constant with tube current from 10 to 30 ma at 15 kv.

The α'' relative intensity as a function of tube voltage is plotted in Fig. 5 and the data are listed in Table II. As the voltage decreases the curve of this figure definitely breaks at about twice the excitaton potential and exhibits the same general features as the voltage function for the intensity of the $K\alpha_{3,4}$ satellites, Fig. 2 of reference 1. This may be taken as evidence that α'' is a satellite line. There can be no doubt that the excitation voltage is less than that which is required to produce a state of KL ionization. This indicates, in view of the conclusions of the previous experiments,[1] that α'' is not of the $\alpha_{3,4}$ group of satellites.

If one assumes that the curve of Fig. 5 should be similar in shape to the curve of the intensity of $\alpha_{3,4}$ *vs.* voltage,[1] one obtains, by the consequent extrapolation to zero intensity, the excitation voltage of α'' as 4070 ± 250 volts. The energy required to remove a K electron of atom $Z=20$ (calcium) is 4030 volts.[18] The energy required to

TABLE II. *The intensity of the Ca $K\alpha''$ satellite line relative to the intensity of the $K\alpha_1$ line as a function of the x-ray tube voltage.*

VOLTAGE	CURRENT (ma)	RELATIVE INTENSITY $(\alpha''/\alpha_1)\times100$
4,500	115	0.80
5,000	89	1.50
5,500	88	1.90
6,500	65	2.15
8,000	57	2.30
10,000	46	2.18
15,000	22	2.30
20,000	15	2.20
30,000	12	2.25

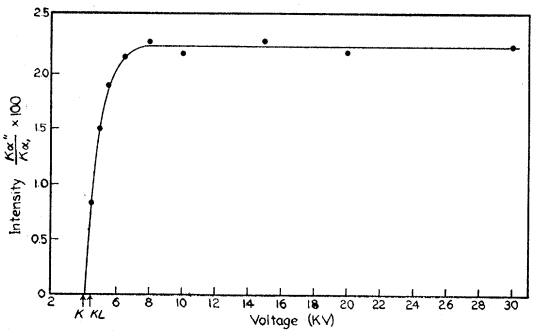

FIG. 5. Intensity of the Ca $K\alpha''$ satellite line relative to the intensity of the $K\alpha_1$ line as a function of the tube voltage. The voltage for which the intensity ratio α''/α_1 falls to zero is the satellite excitation potential. The voltage indicated by K, 4030 volts, is the excitation potential of the $K\alpha_{1,2}$ lines; that indicated by KL, 4440 volts, is the excitation potential of the $K\alpha_{3,4}$ satellites.

[18] M. Siegbahn, *Spektroskopie der Röntgenstrahlen*, second edition (Julius Springer, 1931), p. 348.

remove an $M_{II, III}$ electron of atom $Z=21$ (scandium) is approximately 37 volts. Then the energy requisite to producing a state of KM ionization in the calcium atom is 4067 volts, in excellent agreement with the experimental value.

III. Conclusions

From the excitation potential measurement we conclude that the initial state of the atom emitting the $K\alpha''$ satellite is one of KM ionization, a conclusion which is in agreement with the Wentzel-Druyvesteyn theory and also with the Richtmyer theory for the origin of this satellite.

From the wave-length positions there is no choice between the theories. Druyvesteyn, using Dolejšek's wave-length measurements, has shown[14] that the $\Delta\nu$ interval between α'' and α_1 is of the same order of magnitude as the interval between the frequencies of the M levels of atom $Z+1$ and of atom Z. On the basis of this evidence, Druyvesteyn ascribed, in accord with the Wentzel-Druyvesteyn theory, the origin of the α'' line as due to the transition $KM \rightarrow LM$. In this region of atomic numbers the energy values of the M shells are rather indefinite[18] and by "order of magnitude" must be meant a factor of possibly several-fold. Agreement of about the same order of magnitude is also obtained with Richtmyer's theory.

From the relative intensities, so far as theoretical predictions can be or have been made,[19, 20] there is likewise, as yet, no choice between the two theories.

Acknowledgments

The author is indebted to Professor F. K. Richtmyer for his criticisms of the manuscript and to the University of Chicago for the loan of the double spectrometer with which the data of the present experiments were obtained.

[19] R. D. Richtmyer, Phys. Rev. **49**, 1 (1936).
[20] F. Block, Phys. Rev. **48**, 187 (1935).

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Effect of Intense Illumination on Time Lag in Static Spark Breakdown

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The time lag of spark breakdown in static uniform fields and with *intense* illumination of the cathode has been studied in air, helium and carbon dioxide. An electro-optical shutter was used to observe the time lag, while an auxiliary spark gap supplied the intense cathode illumination. In air, the time lag was about 10^{-7} second for overvoltages of a few percent and increased very rapidly with decreasing overvoltage. Increasing the overvoltage to above 30 or 40 percent reduced the time lag to a more or less constant value of 2 or 3×10^{-8} second. This, in part, is shown to be due to the nature of the initiatory spark. The position of the midgap streamer observed in previous experiments has been found to depend on both the overvoltage and intensity of illumination. An explanation of these observations is advanced on the basis of space charge effects. The results in carbon dioxide were quite similar to those in air. In helium a much higher overvoltage was found necessary to produce a given time lag than in air. This is explained by considerations of the relative rates of gain of energy by electrons in the two gases.

Introduction

THE time lag of spark breakdown in static fields has been studied in a thorough and systematic manner by Zuber[1] and Tilles[2] for lags from about 1 second to below 10^{-5} second. The effects of overvoltage and intensity of illumination of the cathode on the time lag were investigated. Time lags down to about 2×10^{-7} second with low overvoltage and high illumination intensity have been observed by Snoddy.[3] Very short time lags of the order of magnitude of

* Now with Research Corporation, New York.
[1] K. Zuber, Ann. d. Physik **76**, 231 (1925).
[2] A. Tilles, Phys. Rev. **46**, 1015 (1934).
[3] L. Snoddy, Phys. Rev. **40**, 409 (1932).