EXCITATION PROCESSES IN THE HOLLOW CATHODE DISCHARGE

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Abstract

The low potential gradients in the negative glow in a hollow cathode discharge in a rare gas make it a favorable source for the excitation of metallic spark spectra. The metal studied forms the cathode, and is brought into the discharge by cathode sputtering or evaporation. The excitation is limited by collisions of the second kind between gas and metal atoms and ions. The spectroscopic data of all the available cases have been examined to see what determines the processes occurring. In general only those processes occur in which the metal can be excited to some term in the spark spectrum with gain or loss of only a small amount of kinetic energy to balance the reaction equation. High melting point metals or those which sputter poorly cathodically enter the discharge in helium in the normal state or in a low metastable state of the atom. With low boiling points metals appreciable numbers of metal ions enter the reactions. In intermediate cases or in argon or neon, it is not always possible to predict if metal ions will enter the reaction or not. The conditions which determine the results are discussed.

THE excitation of metallic spectra by the discharge in a hollow cathode tube in a rare gas atmosphere has been discussed by Paschen,[1] Frerichs[2] and Takahashi.[3] While there is general agreement that the excitation is mainly limited by collisions of the second kind between rare gas atoms or ions and metallic atoms or ions there has not been agreement as to the exact nature of the collisions. Paschen and Frerichs have attributed the fundamental process to collisions between metallic ions and excited metastable rare gas atoms. Takahashi on the other hand considers only normal or metastable metallic atoms which receive energy from metastable atoms or ions of the rare gases. On the basis of somewhat more experimental material than was available at the time the discussions mentioned above were written, it is now possible as will be shown in this paper to explain the processes involved somewhat more fully and to show that under suitable conditions any of the excitations proposed by the author's mentioned may occur.

The conditions on the hollow cathode are rather different from those in other discharges. With such a cathode, often though not necessarily inside a cylindrical anode, and an applied D.C. potential of 300 or 400 volts, at a suitable pressure which depends on the cathode dimensions, the discharge is almost wholly inside the cathode. The discharge then consists of a negative dark space close to the inner wall of the cathode and a very bright negative

[1] Paschen, Sitzungsb. d. Preus. Akad. d. Wiss. p. 207 (1927).
[2] Frerichs, Ann. d. Physik **85**, 362 (1928).
[3] Takahashi, Ann. d. Physik **3**, 49 (1928).

glow filling the cathode. The positive column practically disappears. This discharge was first used as a spectroscopic source by Paschen.[4] It was explained by Günther-Schulze[5] who showed that when the pressure was decreased in such a tube until the mean free path of electrons leaving the inner wall of the cathode was sufficient to bring them into the positive space charge of the opposite side of the inner wall they would there reduce this charge causing an increased current and a lower cathode fall of potential inside and so setting up a condition permitting a very much greater current density from the inner wall of the cathode than from the outer. The discharge then takes place chiefly inside the cathode. The pressure at which this effect will occur depends on the diameter of the cathode and the nature of the gas. It is a pressure such that the normal cathode dark space is about equal to the inner radius of the hollow cathode. The discharge however is formed inside the cathode with an abnormal dark space thickness much less than normal. This space inside the negative glow of the hollow cathode is nearly field free and ions may exist there in considerable concentrations and radiate freely even from states of high quantum number. The negative glow in the hollow cathode is very brilliant and this light source is one of the best for exciting the first spark spectra of the metals.

The metallic atoms which enter the discharge are removed from the cathode wall by ionic bombardment and evaporation. In the analogous case of cathode sputtering Von Hippel[6] found with argon at 0.1 mm pressure in spectrograms of the light just at the cathode surfaces that the only spectral lines of the cathode material which appeared were the resonance lines of the atom. From this he concluded that the material is given off in an atomic state and arrives in the negative glow by a diffusion process. His theory is that intense local heating of the cathode by ion bombardment causes minute hot spots from which the cathode metal is evaporated. If the resonance lines of the cathode metal appear near the cathode, the cathode metal must enter the discharge as excited atoms as well as normal atoms. Ions knocked off the cathode could not normally penetrate the high cathode fall of potential in the hollow cathode (100–300 volts according to measurements of Schüler).[7] We may expect in general in the negative glow of the hollow cathode reactions with metallic atoms both neutral and excited (in metastable states) although, as will be pointed out later, under certain conditions significant numbers of metal ions may enter the reactions. These metallic particles entering the negative glow suffer collisions with rare gas particles, or with electrons whose velocity is limited by collisions with rare gas atoms. The spectrum of the negative glow shows the spectrum of the ionized exciting gas very strongly. In fact with a grating not particularly good below λ300 Sawyer and Lang[8] observed in the discharge in helium as many as four

[4] Paschen, Ann. d. Physik **50**, 901 (1916).
[5] Günther-Schulze, Zeits. f. Physik **19**, 313 (1923).
[6] v. Hippel, Ann. d. Physik **80**, 672 (1926) and **81**, 1043 (1926).
[7] Schüler, Phys. Zeits. **22**, 264 (1921).
[8] Sawyer and Lang, Phys. Rev. **34**, 712 (1928).

members of He II series 1^2S-m^2P beginning at λ304 and Paschen[9] under suitable pressure and current conditions has observed in the hollow cathode in helium Stark effect in the higher members of the helium series due to the electric fields of the great concentration of helium ions. It is then to be expected that excited atoms in the metastable state and ions in the normal state will be the predominating energy states in which the rare gas will be found and that the transfer of these energies to the metallic atoms will fix the limiting conditions of excitation for the spectrum of the metal.

To check these considerations there are available data for the hollow cathode excitation of aluminum, copper, magnesium and zinc in helium, argon and neon; cadmium in helium and argon; and gallium, mercury and thallium in helium.[10] Not all of these data are well adapted for the study of the question in hand. In some cases the investigation did not cover a sufficiently wide spectral region to permit a certain determination of the kind of excitation attained in the discharge. In others the limit attained is low and so the terms too few and too far apart to fix the limit sharply. For the sake of completeness it has, however, all been assembled.

TABLE I. *Important energy levels of metallic spectra.*[11]

	Normal State of Atom			Metastable State of Atom			Normal State of Ion		
	Config.			Config.			Config.		
Al	(s^2p)	$^2P_{\frac{1}{2}}$	42280	—	—	—	(s^2)	$^1S_0$	151860
Ga	(s^2p)	$^2P_{\frac{1}{2}}$	48379	(s^2p)	$^2P_{1\frac{1}{2}}$	47552	(s^2)	$^1S_0$	165458
Tl	(s^2p)	$^2P_{\frac{1}{2}}$	49263	(s^2p)	$^2P_{1\frac{1}{2}}$	41470	(s^2)	$^1S_0$	164600
Mg	(s^2)	$^1S_0$	61663	(sp)	$^3P_0$	39813	(s)	$^2S_{\frac{1}{2}}$	121265
Cu	$(d^{10}s)$	$^2S_{\frac{1}{2}}$	62306	(d^9s^2)	$^2D_{2\frac{1}{2}}$	51105	(d^{10})	$^1S_0$	163634
Zn	$(d^{10}s)$	$^1S_0$	75759	$(d^{10}sp)$	$^3P_0$	43450	$(d^{10}s)$	$^2S_{\frac{1}{2}}$	144890
Cd	$(d^{10}s^2)$	$^1S_0$	72535	$(d^{10}sp)$	$^3P_0$	42420	$(d^{10}s)$	$^2S_{\frac{1}{2}}$	136377
Hg	$(d^{10}s^2)$	$^1S_0$	84182	$(d^{10}sp)$	$^3P_0$	46536	$(d^{10}s)$	$^2S_{\frac{1}{2}}$	151280

For each of the metals mentioned above Table I gives the electron configuration of the normal state of the ion and of the first state and of the lowest metastable state of the atom. In aluminum this metastable state is the lowest $^2P_{1\frac{1}{2}}$ of the normal configuration and is too near $^2P_{2\frac{1}{2}}$ to be differentiated in the data at hand. Table I also gives for each configuration the energy of removing the outermost electron from this configuration—that is to excite the metal to the lowest or normal state of its next ion. For con-

[9] Paschen, Sitzungsb. d. Preus. Akad. d. Wiss., p. 135 (1926).

[10] Al in He, Sawyer and Paschen, Ann. d. Physik. **84**, 1 (1927).
Hg in He, Paschen, Sitzungsb. d. Preus. Akad. d. Wiss., p. 3 (1928). and Naudé, Ann. d. Physik **3**, 1 (1929).
Cd and Zn in He, Takahashi, Ann. d. Physik **3**, 27 (1929).
Tl in He, Smith, Phys. Rev. **35**, 235 (1930).
Ga in He, Sawyer and Lang, Phys. Rev. **34**, 712 (1928).
All others, Frerichs, Ann d. Physik **85**, 362 (1928).

[11] The data in table II are taken from Paschen-Götze "Seriengesetze der Linienspektren" or from the references in footnote 10.

venience in spectroscopic discussion this value is given in ν-units. It may of course be converted to equivalent volts by multiplying by 1.2345×10^{-4}. For the three rare gases the atomic energies available are, also in ν-units

	Energy of ionization	Energy of metastable state
Helium	198308	159830 (2^3S) or 166251 (2^1S)
Neon	173930	134819
Argon	127104	94546

From the energy available from the rare gas atoms together with the data of Table II there may be calculated the highest spectroscopic state of the metal ion which should be excited by any of the probable collisions of the second kind with a rare gas. Thus for example $Zn'(d^{10}sp\,^3P_0)+He'(2^3S)\rightarrow Zn^+(?)+He(1^1S)+e$ we have:

energy to ionize metastable zinc	43450
energy to doubly ionize first zinc ion	144890
	188340
energy of He (2^3S)	159830
	28510

Thus, this reaction fails by 28510 ν-units to achieve second ionization, or a Zn II term of absolute value (measured from ionization) 28510 would just be excited. The results of such computations are listed in Table II, where in the column heads M stands for the metal concerned and G for the gas. Reactions with He' (2^1S) are not listed. The results of a reaction with He' (2^1S) may be obtained by subtracting 6421 from the term obtained by a reaction with He' (2^3S).

TABLE II. *Excitation of metallic spectra in hollow cathode discharge in gases.*

	Calculated		–	Excitation		–Observed	
	M+G'	M+G$^+$	M'+G'	M'+G$^+$	M$^+$+G'	Maximum	Limit
Al+He	40310	*1832*	—	—	−7970		1116
+Ne	65321	26210	—	—	*17041*		16943
+A	105594	73036	—	—	*57314*		56512
Ca+He	54007	*15529*	53180	*14702*	5628		12397
Tl+He	54033	*15555*	46240	7762	4770		12484
Mg+He	23098	−15380	*1248*	−37230	−38565		5419
+Ne	48109	*8928*	26259	−12922	−13534	8−10000	5419
+A	88382	55824	66532	33974	26719		17844?
Cu+He	66110	27632	54909	*16431*	3804	27−30000	16703
+A	131394	98836	120193	87635	*69088*		68837
Zn+He	60819	*22341*	28510	*−9968*	*−14940*	22−28000	−11400
+A	126103	93545	93794	61236	50344		27800?
Gd+He	49080	*10602*	18967	−19510	*−23453*	11−13000	−26800
+A	114364	81806	84251	51693	41831		46531
Hg+He	75632	*37154*	*37986*	−492	*−8550*	39−42000	−8019

The processes in italics are those which account for observed features of the spectra.

The experimental results of interest in this discussion are tabulated in the two right hand columns of Table II. In each case where it is certainly determined there is given the limit, that is, the highest spectral term of the metal ion excited in the rare gas atmosphere. There is also given any observed maximum of excitation—any terms which appear to be excited more strongly than immediately lower terms—indicating resonance phenomena in the exciting process.

A comparison of the calculated and observed excitation in Table II shows that many of the observed features of the spectra may be explained on the basis of various of the exciting processes. The cases will be discussed in order of their simplicity.

Aluminum, gallium and thallium are all high boiling point metals. Aluminum sputters cathodically less than any other metal tried. Consequently the concentration of these metals in the hollow cathode discharge in helium is very low; they react only as normal atoms or possibly in the case of gallium and thallium as atoms in the very low metastable $^2P_{1\frac{1}{2}}$ state. The limit is clearly set in the case of excitation in helium by $M+G^+$ or $M'+G^+$. There are no resonance maxima in these cases because, although the process $M+G'$ must contribute to the excitation, the limit of this excitation falls where the spectral terms are not numerous enough nor close enough together to make such a maximum apparent.

In the case of aluminum in argon and neon a new effect enters. The limit here is obviously set by $M^+ + G'$. That is, metal ions are entering this discharge although the concentration of metal in these cases is still so small that metal ions are not to an appreciable extent current carriers, as does occur in cases to be mentioned later. The greater number of metal ions is here due probably to the heavier bombardment of the cathode by the heavier gas particles. A similar effect appears in the vacuum spark where increased voltage on the spark giving heavier bombardment of the electrodes brings higher ionized atoms into the spark.

The limit of excitation for magnesium in helium and neon appears to be set respectively by the reactions $M'+G'$ and $M+G^+$, although these cases have perhaps not been investigated over a sufficiently wide spectral range for absolute certainty as to the limit.[2] In the neon the excitation goes somewhat (1/3 volt) above $M+G^+$ and a maximum corresponding to resonance with this process in the series $3^2D - m^2F$ is clearly seen. The energy for overshooting of the limit, $M+G^+$, probably comes from kinetic energy of the atoms. The process, $M^+ + G'$, which sets the limit for Al+Ne probably does not occur here. It would call for excitation 13235 cm^{-1} beyond double ionization and as negative terms in Mg II are not possible and as there are no terms in Mg III as low as this, this process would involve freeing an electron with this surplus energy—a process which seems improbable. It will be seen that for magnesium and argon the limits of the five different processes are well separated and all positive. However, this case is not so favorable for observation as it seems for most of the limits are too low in the Mg II spectrum to allow maxima of excitation to be observed. It will

be noted from Table II that Frerichs observed excitation 10256 cm^{-1} above the highest limit. It is not clear how this can occur. A similar anomaly occurs with zinc in argon but in no other observed cases. It may be that here the reaction is with some high excited state of the metal atom but what state could occur with sufficient probability is not obvious.

Copper should offer an excellent opportunity to study excitation conditions in the rare gases since all the processes give rise to positive terms in Cu II. The copper spectrum is, however, unfortunately not completely analyzed and the combinations of the highest known terms lie largely in the extreme ultra violet. The highest term found by Kruger in helium, however, seems clearly to arise from $M'+G^+$. The process $M+G^+$ is responsible for a maximum of intensity found by Kruger for terms from 27–30000 cm^{-1}. Frerichs' work in neon did not lead to determination of any limit, but in argon the limit is set by M^++G' again, as with aluminum in neon and argon.[12]

Zinc, cadmium and mercury represent a different type of excitation condition. These metals have low boiling points and relatively high vapor pressure at the cathode temperature in the hollow cathode discharge. The ions of these metals enter the discharge in such concentrations as to carry a considerable part of the current. In fact in mercury the discharge may be operated without any rare gas using a carbon cathode and allowing the heat of the discharge to vaporize the mercury. Under such conditions we may expect that in all cases where the process M^++G' gives rise to actual terms that this reaction will set the limit to the excitation. This is indeed the case as will be seen by reference to Table II. In all these metals negative terms in the spectrum of the ion are possible and have been found so that the excitation has been traced to the highest limit permissable in helium. In zinc and cadmium the limit given in Table II is in fact exceeded by 3000 ν-units. This is possibly due to reaction with the higher metastable helium term (2^1S) which as pointed out previously would give excitation 6000 cm^{-1} higher than 2^3S which is given in the table. In the spectra of all these three metals some unclassified lines remain and more negative terms may be found to reach the limit M^++He' (2^1S). In helium with each of these metals there is also found maxima of excitation explainable as resulting from $M+G^+$ which appears in these cases to be more probable than $M'+G'$ no doubt because M' is so high in these metals that it is less likely to be excited strongly than in the case of copper or magnesium. The metals have not been studied in neon with the exception of zinc where, however, the spectral range covered by Frerichs was not sufficient to permit conclusions to be drawn. In argon, however, the limit is clearly set by M^++G' with cadium while with zinc, as mentioned above, even this limit which is the highest set by the simpler reactions, is exceeded by 25000 cm^{-1}. This, as in the case of Mg+A, does not appear susceptible to obvious explanation.

[12] Frerichs terms have been corrected to the true lowest term in Cu II not known at the time of his work.

In conclusion it may be said that the excitation of metallic spectra in the hollow cathode discharge in rare gases does not give results which are entirely predictable. In general with metals which do not sputter too freely nor have too high vapor pressures at the cathode temperatures, as Mg and Al, the reaction $M+G^+$ together with $M'+G'$ and $M'+G'$, if M' is low, will occur, and the highest of these will set the limit to the excitation if this does not call for non-existent negative terms. With such metals in neon or argon M^++G' will in general occur due to the greater kinetic energy with which they bombard the cathode. With metals of high vapor pressure, as zinc, cadmium or mercury, M^++G' will always set the limit if the terms called for are possible—i.e. not impossible negative terms.

While the limit of excitation will be set by whichever of the possible processes, as described above, possesses the greatest energy which the metal atom or ion can absorb, the processes leading to lower excitations will manifest themselves by maxima of excitation of the terms with which they are nearly in resonance, providing these excitation levels fall where the M^+ terms are close enough together for such maxima to be distinguishable.

For metals intermediate between the types above discussed it does not appear on the basis of present information possible to predict the excitation conditions. Whether or not metal ions will play a conspicuous part in the excitation will apparently depend too much on current density, cathode temperature and gas pressure in particular cases. Altering any of these may influence widely the character of the discharge. It would seem that by placing the metal in a carbon cathode whose temperature could be controlled by the discharge current density or by external heating, it should be possible to pass at will, by varying the vapor pressure of the metal and the gas pressure from the case of low vapor pressure with $M+G^+$ as limit to that of high vapor pressure with M^++G' as limit. A complete theory of the discharge under all conditions and for all gases and metals is not yet possible.