THE EMISSION OF NEGATIVE IONS UNDER THE BOMBARDMENT OF POSITIVE IONS

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Abstract

The results which Sawyer obtained from the reflection of lithium ions from reflectors of platinum foil and nickel crystal deposited on tungsten, indicated two distinct angles at which reflection occurs more strongly than at other angles, one coming nearly at the angle of specular reflection as found by Read and Gurney, and the other which appeared only at relatively high voltages, at an angle approximately normal to the reflecting surface. Experiments made by reflecting the lithium ions from a metal surface in a field free space gave the bundle at the specular angle as before, but no trace of a bundle at the normal to the surface could be found. When a field is applied so as to retard reflected positive ions there was evidence of negative emission coming from the target under the bombardment of lithium ions. A magnetic analysis system was set up to determine the nature of the negative charges. Negative fluorine, chlorine, oxygen and sulphur ions were obtained by bombarding NaF, CaF_2; NaCl, CaO, PbS and oxide-coated vacuum tube filaments. Clean metal targets of platinum, gold, aluminum, tantalum, nickel, and tungsten were found to emit electrons and the negative ions H_1^-, H_2^-, OH^-, and Cl^- with traces of what is probably N^- and $LiOH^-$. The strongest bundles were the first four which indicate that water-vapor molecules were broken up into their components.

Introduction

THE results which Sawyer[1] obtained from the reflection of lithium ions reflected from reflectors of platinum foil and nickel crystals deposited on tungsten, indicated two distinct angles at which reflection occurs more strongly than at other angles, one coming nearly at the angle of specular reflection as observed by Read[2] and Gurney[3] and the other, which appeared only at relatively high voltages, at an angle approximately normal to the surface of the reflector. This latter beam was observed when the reflection took place in strong electrostatic field. The present investigation developed out of a further study of this normally reflected beam. It was suspected from these experiments that the observations were complicated by a new type of emission, namely the emission of negative ions from metal surfaces under the bombardment of positive ions. The second part of the paper describes a direct investigation of this new phenomenon and gives an analysis, by the methods used for positive rays, of the types of negative ions obtained in this way.

Part I

The tube used in the first experiments on reflection of positive ions by metals was the one described by Sawyer modified somewhat as shown in Fig.

[1] R. B. Sawyer, Phys. Rev. **35,** 1090 (1930).
[2] G. E. Read, Phys. Rev. **31,** 629 (1928).
[3] R. W. Gurney, Phys. Rev. **32,** 467 (1928).

1. In this a strip of platinum foil *F* carrying a small crystal of spodumene on a constricted portion served as a source of positive ions when heated electrically. After heating to a yellow heat for several minutes the emission is practically all lithium ions. These ions are drawn to the drum *D* by a potential applied from the outside of the tube. The collector *C* was a small Faraday chamber subtending an angle of about 9 degrees from the target *T*. It was supported by a stiff wire insulated from the rest of the apparatus. Connection to the electrometer was made through very flexible nickel ribbon wound like a clock spring. The whole collector system was very carefully shielded from any possible ions escaping from the filament by enclosing the collector in a hood, and by a disk which covered the end of the cylinder *H* and extended beyond the guard ring *G*. The collector and cylinder were rotated on a common axis by means of an electromagnet applied from the outside to the arm-

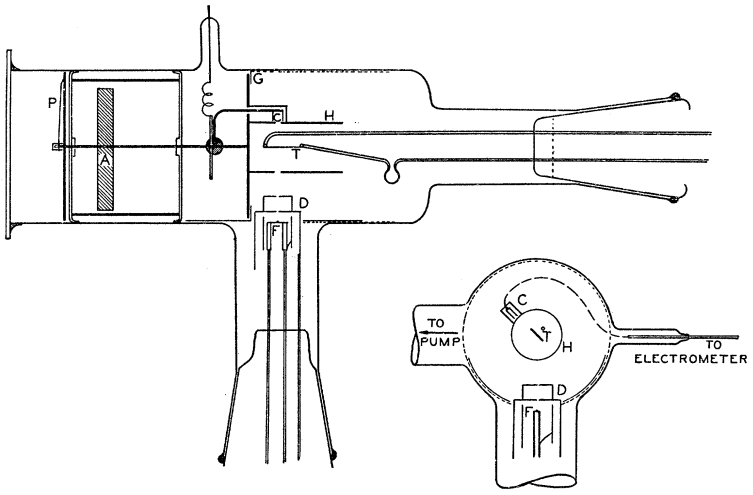


Fig. 1.

ature *A*. The angle reading could be made through the Pyrex window with the pointer *P* on the scale.

The target *T* on which the lithium ions fell, was a strip of platinum foil about 0.3 cm wide and 1 cm long. It was held in place by two leads, one of which was flattened and bent to serve as a spring to keep the target taut. The other was placed behind the target to reduce field distortion. A piece of nickel gauze was put over the slit in the cylinder *H* in the region of the collector in order to reduce the distortion of the field.

As the target and filament had to be changed frequently two ground joints were used, that were sealed by a ring of picein cement about the outer edge. No difficulty was experienced with contamination of the target, as it was kept at a low red heat throughout the observations.

To examine the reflection in its simplest form the ions were allowed to strike the target in a field free space. This was done by applying an accelerating potential between the filament and drum, and the retarding potential be-

tween the cylinder and collector. When the positive ions were reflected in a field free space the peak at the angle corresponding to specular reflection appeared as before, but no trace of a peak at the normal could be found. This was true in the apparatus used by Sawyer, and also in the modified form which differed only in the use of a Faraday chamber as a collector, which was shielded in front by a nickel gauze in order to avoid all electric fields in the reflecting chamber. In the case of Sawyer's experiments the potential was applied partly between the filament F and the drum D and partly between the cylinder H and target T, the drum and cylinder being at the same potential. The cylinder to target potential served as an accelerating voltage for the incident ions, and at the same time as a retarding potential for the same ions after reflection.

It was also found that when the gauze was put over the slot in the cylinder, and a retarding field for positive ions was applied between the target and cylinder, there was evidence of negative charges coming to the collector when it was nearly normal to the target. In one instance a negative potential of 28 volts had to be applied to the collector to prevent it from collecting negative charges which are then presumably deflected into the gauze. Since the specular bundle remained positive as before, it is reasonable to assume that the negative ions were formed on the target and accelerated to the cylinder by the field that retarded the reflected positive ions.

To compare the sharpness in angle of a beam of ions liberated at the target with the negative beam actually observed, a bit of spodumene was put on the target and heated. With no accelerating voltage some of the positive ions found their way to the collector, but with a few volts accelerating potential a very narrow intense beam was observed. This indicates that the field at the surface of the target is normal to it and is strong enough to form a beam strongly concentrated in the normal direction.

Attempts to eliminate the negative charges, obtained by bombardment of the target, by putting an electromagnet around the tube in such a way as to deflect them away from the collector were unsucessful. The nickel shields may have weakened the magnetic fields to a certain extent but the insensitiveness of the negative charges points to the emission being ionic rather than electronic in nature.

Although we may explain the negative charges observed near the normal to the target as due to secondary negative ions set free by bombarding positive ions, the reflected positive ion bundle which Sawyer observed is more difficult to explain. Since the beam occurs only when the field is strong inside the cylinder the concentration of the ions at the normal is probably due to the field itself. It may be that, since the target is wide in comparison to the diameter of the cylinder, the lines of force are in such a direction that ions reflected from the center of the target would be reflected specularly, while those striking the target nearer the edges would be drawn toward the normal, after reflection, by the field.

PART II

To identify the negative charges freed from a metal surface by positive ion bombardment and to see whether they are electrons or ions a Dempster[4] magnetic analysis system was set up as shown in Figs. 2 and 3. A filament F coated with spodumene was made positive with respect to the target T supported above it. Any negative ions formed at the target would be accelerated downward by this same potential. Some of them would go by the edge of the filament and pass through the slit S into the magnetic field. With a stream of ions of the same mass and the same velocity a value of the magnetic field

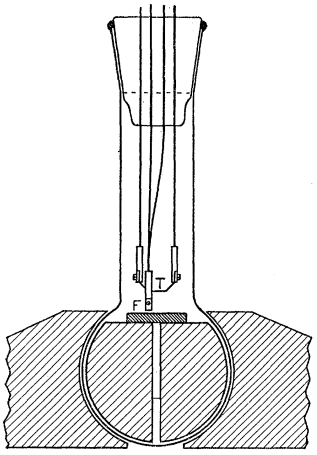


Fig. 2.

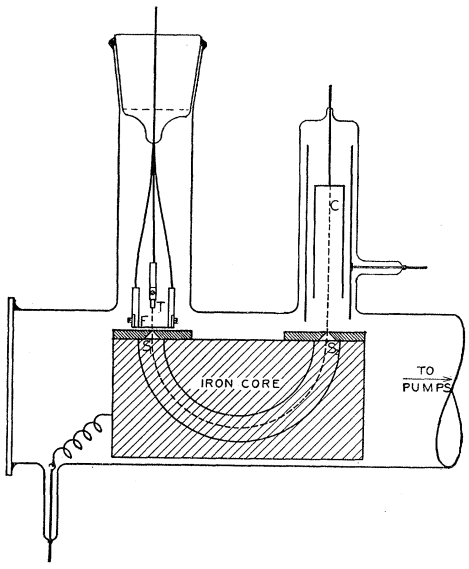


Fig. 3.

could be found that would deflect them through a semi-circle and allow them to pass out through the other slit S to the collector C.

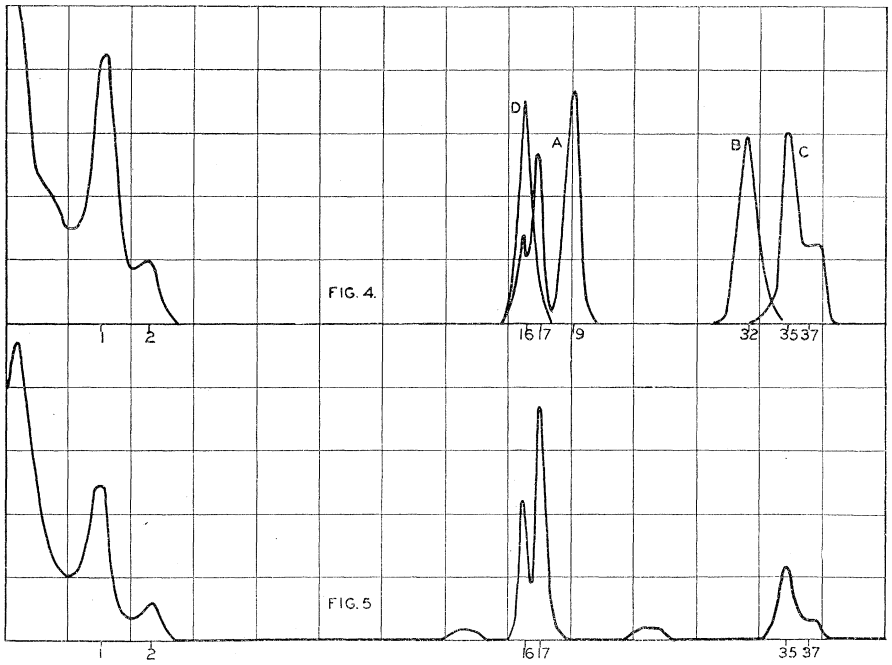
The first results with the apparatus gave a considerable negative ion emission, but the resolution was not good enough to separate definite ion bundles. At this time the experiments were interrupted, but Dr. J. S. Thompson kindly undertook to carry out the analysis of the ions. He introduced some improvements in the apparatus, such as the shield about the collector, which greatly improved the resolving power. With the improved apparatus he was able to demonstrate the emission of negative ions and to identify several distinct negative ion bundles.[5]

Experiments were later resumed by the author with the same apparatus to study further the different kinds of ions that may be obtained in this way. To avoid uncertanty in identifying the ions the slits were narrowed to 0.8 mm and the apparatus calibrated by means of positive ions that were accelerated

[4] A. J. Dempster, Phil. Mag. **7** Series 13, 115 (1926).
[5] J. S. Thompson, Phys. Rev. **38,** 1389 (1931).

at various potentials. When heated, spodumene liberates positive ions of lithium, and traces of sodium, and potassium according to other investigators[6] and these ions are brought to the collector successively as the field strength in the iron armature is increased. Assuming the magnetic field to be symmetrical when the magnetizing current is reversed, the mass of the negative ions may be deduced. Later the calibration was checked by the use of negative fluorine ions.

Richardson[7] finds that negative ions are obtained from iodides, chlorides, bromides, and fluorides by heating their salts. Barton[8] found negative ions of mass 33 to be liberated from the oxides of strontiun and barium when heated.



Figs. 4 and 5.

This suggested that electronegative ions might be obtained from the bombardment of their salts by positive ions. The negative ions obtained by bombarding various salts are shown in Fig. 4. The ion intensity is plotted against the magnetizing current. Fig. 4A shows the negative ions obtained by bombarding NaF or CaF_2 with 500 volt lithium ions. The ion at 19 does not appear at all when the platinum target is clean, but appears with great intensity when the target is covered with the fused fluoride salt, thus definitely associating the peak with the negative fluorine ion. The method of applying consists of wetting the surface of the target with a solution of the salt. As the target is

[6] J. L. Hundley, Phys. Rev. **30**, 864 (1926).
[7] O. W. Richardson, Emission of Electricity from Hot Bodies. p. 107.
[8] H. A. Barton, Phys. Rev. **26**, 360 (1930).

slowly heated the water evaporates leaving a fine layer of salt on the target, which can be fused by further heating. CaF_2 could not be dissolved in water but was powdered and the powder dusted on the target with a bit of cotton, then fused by heating. A thick film is undesirable as there may be considerable voltage drop through it. No negative ion emission was obtained by simply heating the target, that was strong enough to observe by the methods used in these experiments.

The ions obtained by bombardment of NaCl fused to the target are shown in Fig. 4C. Considerable intensity was obtained when the target was cold, but in common with other salts, the emission was stronger when it was heated. The ions show the doubling to be expected from the isotopic nature of chlorine and the agreement with 35 and 37 is very good. No chlorine ions were observed when the bombarding ion current was cut off and the target heated only. The method of applying this salt to the target by evaporating a solution of it on the target surface does not work out well in this case, since the salt crystals explode when they lose their water of crystalization. A small hood held over the target effectively holds the escaping crystals until they have been fused. Richardson[7] found that negative ions were obtained by heating manganous chloride that had molecular weights between 59 and 88, showing that the ions were of atomic or molecular magnitude and possibly molecular chlorine. Barton[9] found a few negative chlorine ions from HCl formed either by bombardment with low velocity electrons or from thermal dissociation at a hot filament.

In Richardson's experiments there are no records of negative ions of the elements in the sixth column of the periodic table. Barton[8] thought his ion of mass 33, which was obtained from heating barium and strontium oxides, might be due to molecular oxygen. He found no negative atomic oxygen however as might have been expected. The question as to whether negative atomic oxygen is freed from its compounds under positive ion bombardment was investigated by depositing calcium oxide on a platinum target. On bombarding it with lithium ions the negative ion bundle shown in Fig. 4D was obtained. It could be identified definitely from the calibration curve as having a mass 16. Although molecular oxygen (32) was looked for, no trace of it could be found. The impacting ion evidently frees atomic oxygen which is drawn to the collector before it has a chance to combine with another atom to form a molecule.

When a commercial oxide-coated vacuum tube filament was used as a target, negative ions of atomic oxygen gave a strong peak when the filament was bombarded with lithium ions. Before it had been heated it gave in addition a more intense bundle at mass 17, but this disappeared when the target was heated, leaving only the peak at 16. The oxide coated strip was then activated by heating to a yellow heat for several minutes an applying a potential until a strong emission of electrons was obtained. The negative ion emission from it, by bombardment, then gave the two peaks at 16 and 17 in the same pro-

[9] H. A. Barton, Phys. Rev. **30**, 614 (1927).

portions as before it had been heated. This indicates that moisture remains in the oxide coated filaments even after they have been heated to a bright yellow heat and "activated" by drawing electrons from them for some time.

The emission of negative oxygen ions from oxides, by bombardment, suggested that sulphur ions might be obtained from sulphides. PbS was powdered and fused to a clean platinum target, great care being taken not to decompose the substance. When bombarded with the positive lithium ions no effect was produced until the target was heated, then the peak shown in Fig. 4B appeared with a mass 32. No negative ions are emitted when the bombarding ion current is cut off even through the target is hot. Schmidt[10] finds no ions up to a temperature of 450°C by the heating of PbS. We conclude then that the bombardment of lithium ions dissociates the hot sulphide and frees negative ions of sulphur.

When ever any of the substances examined were bombarded with positive ions we get in addition to their characteristic ion bundles several distinct peaks as shown in Fig. 4 to the left. The peak nearest the axis is due to electrons and varied in intensity somewhat. The peak at mass 1 was very strong and a much weaker peak appeared at mass 2. These are evidently H_1^- and H_2^- that have been knocked out by the impinging positive ions, probably from water vapor contained in the salts.

From the negative ions, produced as described above, a calibration of the magnet was made which checked approximately with the positive ion calibration, but showed that the magnetic field was not absolutely symmetrical on reversal.

In addition to the clean platinum target used by Thompson targets of aluminum, gold, tantalum, nickel and tungsten were bombarded with positive ions. The negative ion beams emitted by these various metals resemble each other closely, indicating that the emission is independent of the metal of the target. A typical negative ion "spectrum" is shown in Fig. 5. The strong emission near the axis occurs at a field too weak to deflect anything more massive than electrons. The most prominent peaks occur at exactly 16 and 17 and are unquestionably due to O^-, and OH^-. Another strong bundle occurs at mass 1, with a much weaker one at mass 2. Since these two are probably H_1^- and H_2^- and they occur with O_1^- and OH^- in such large quantities in all metals observed, it appears that the lithium ions must strike water vapor molecules on the surface of the target, breaking them up into their components which are drawn to the collector. The fact that the H_1^- and OH^- bundles are stronger than the H_2^- and O^- bundles seems to support such an hypothesis.

The next strongest negative ion beam comes at 35 and 37 and is unquestionably chlorine since the position and shape of the curve is exactly the same as that obtained when the target is coated with NaCl. Just as any fresh metal will give the characteristic yellow color of sodium when first put in a Bunsen flame, so these negatively charged chlorine atoms appear to be present in all

[10] G. C. Schmidt, Ann. d. Physik **75**, 337 (1924).

metals tested. Prolonged bombardment however makes them disappear. The smaller peaks at 13 and 24 to 25 are much less intense. They do not occur at all in metals that are exceedingly pure and have clean surfaces. After the metal has been bombarded for some time they disappear. Probably they are N_1^- and $LiOH^-$.

The negative ions produced by bombardment of metal surfaces are evidently due to contamination of the target or to adsorbed gases. Cl^-, O_1^- and OH^- ions nearly all disappear from targets such as platinum and tungsten when they are heated to a bright yellow heat for five minutes or more. In distinction to this behavior the emission of ions from oxides, chlorides, fluorides and sulphides persists as long as the salt remains on the target.

In the experiments described above the potential between the target and the filament was 500 volts. An attempt was made to find a critical voltage below which the negative ions were not freed from the target by bombardment, but no critical lower potential could be observed. The intensity of the negative ion beam decreased rapidly as the voltage was reduced, but some negative ions were observed as low as 50 volts.

In conclusion the writer wishes to acknowledge his indebtedness and express his appreciation to Professor A. J. Dempster who proposed the problem and whose suggestions for its development have been invaluable. The writer also wishes to thank Dr. R. B. Sawyer and Dr. J. S. Thompson for their cooperation and valuable assistance.