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Filament Sources of Positive Ions

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Efficient filament sources of ions of the alkali metals have been produced by heating synthetic alkali aluminum silicates. Studies of emission of the lithium sources as a function of composition reveal that the silicate 1 Li_2O : 1 Al_2O_3 : 2 SiO_2 is the most satisfactory ion emitter. Similar sources of the other alkalies prove stable and copious. Ions of Mg, Ca, Sr, Ba, Al, Ga, In, Ti, V, Mn, Y, and Ce, are emitted when the oxide of the metal in question is heated to a white heat on a tungsten filament. The O_2^- peak observed by Barton has been checked. In the case of aluminum, negative ions of mass 27—presumably Al^-—were observed.

INTRODUCTION

A NUMBER of methods are known by which ions can be produced in sufficient quantities for mass spectrograph analyses. If the substance to be studied can be used as a vapor, it is a simple matter to produce ions by collisions with slow electrons. For production of ions of solid substances, several gas discharge methods are available, in particular the very fruitful "anode-ray" method used by Aston. However, it has proved difficult in many cases, for instance with the alkaline earths, to obtain ions in large quantities. Still another method for the production of positive ions is the hot filament, and it is with this type of source that the present paper is concerned. The emission of positive ions from hot filaments is a well-known phenomenon, discussed at some length by Richardson[1] as long ago as 1916. It has been studied mainly from the point of view of determining what ions are emitted from various compounds; glass, for example, has been a favorite object of study. But there have been very few attempts to develop filament sources of ions of particular elements. Perhaps this is because the absence of multiply charged ions is a drawback in using such sources for the study of isotopes. Nevertheless some good results have been obtained by this method[2] and in the hope that copious filament ion sources may be valuable both in measurements of relative abundance of isotopes and in the accurate determination of masses, we undertook the work reported in this paper. We have attempted to develop sources that are fairly copious and whose emission is reasonably free from ions of other elements. Except in two or three cases, no claim can be laid to the discovery of new types of emission. Nevertheless, it is hoped that the methods described here may prove useful, not only in mass spectroscopy, but also in other branches of research which deal with phenomena associated with beams of positive ions.

APPARATUS

The substances whose emission was to be studied were coated on filaments which took the form either of platinum strips or mesh, or of tungsten spirals. They were about 15 mm long and 1 to 2 mm in width and were heated directly. The techniques employed in preparing the filaments will be described below in connection with the particular materials investigated.

The ion beams were analyzed in the Dempster type mass spectrograph described by one of us[3] in connection with the analysis of bromine. The ion source described there was removed, and a filament source consisting of the filament under consideration and a drawing out slit was inserted behind the analyzing slit. A constant drawing out voltage of 100 volts was applied between filament

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[1] O. W. Richardson, *The Emission of Electricity from Hot Bodies* (Longmans Green and Co., London, 1916), second edition, 1921, Chap. VIII. For a more up-to-date discussion and bibliography of this type of work see Reimann *Thermionic Emission* (Wiley, New York, 1934), Chap. VI, or Jones, *Thermionic Emission* (Methuen, London, 1936), Chap VI.

[2] Cf. Dempster, Phys. Rev. **11**, 316 (1918); Barton, Harnwell and Kunsman, Phys. Rev. **27**, 739 (1926); Kunsman, J. Frank. Inst. **203**, 635 (1927); Cottrell, Kunsman and Nelson, Rev. Sci. Inst. **1**, 654 (1930); Bainbridge, J. Frank. Inst. **212**, 317 (1931); Powell and Brata, Proc. Roy. Soc. **A141**, 463 (1933).

[3] Blewett, Phys. Rev. **49**, 900 (1936).

and first slit, and the analyzing voltage of 300–500 volts was applied between the first slit and the analyzing slit. The filament and drawing out slit were supported on a ground glass joint which was made vacuum tight with stopcock grease. This arrangement made changing the filament a comparatively simple task. As a rule the filament was mounted across the analyzing slit so that only the emission from a short section entered the mass spectrograph. This method was adopted since an appreciable voltage was required to heat the filament, and if ions from the whole filament entered the analyzer, their energy distribution would considerably decrease the resolving power.

ALKALI ION SOURCES[4]

That alumino-silicates of the alkalies could be used as ion sources has been observed by Hundley[5] and Bainbridge.[2] Preliminary experiments soon proved that these compounds were among the best thermionic sources of ions yet tried. On the basis of these observations it was thought worth while to study the emission of positive alkali ions from the corresponding alumino-silicates in some detail with the object in view of stabilizing and increasing the emission and obtaining some information concerning the mechanism of the process.

Lithium was chosen as the alkali best suited for such a study since the ternary system $Li_2O \cdot Al_2O_3 \cdot SiO_2$ had been studied by several workers,[6] and thus the composition of the various compounds existing in this system are known.

Various compositions were made by melting Li_2CO_3, $Al(NO_3)_3 \cdot 9H_2O$, and pure powdered quartz together at about 1400°C. The melts were then powdered and remelted. The repeated devitrification technique necessary in phase diagram studies was, however, not carried out in this work. After preparation the compounds were examined under the polarizing microscope and were found to consist predominantly (90 percent) of the desired phase. These observations were verified by x-ray photographs.

The compound to be tested thermionically was then powdered and 0.25 g were mounted on a filament of platinum gauze 1 cm^2 in area. Water was used as a binder. The apparatus used has been described elsewhere.[7] The accelerating potential used was 1500 volts so that the current would be approximately emission limited.

The compounds varied widely in their positive ion characteristics. In general the ternary compounds were considerably better than the binary ones. The most satisfactory one of all was β-eucryptite ($1\ Li_2O \cdot 1\ Al_2O_3 \cdot 2\ SiO_2$) which gave at a particular temperature about twice the current as dids podumene ($1\ Li_2O \cdot 1\ Al_2O_3 \cdot 4\ SiO_2$). Currents as great as 1.0 milliampere were readily obtained from β-eucryptite at a temperature 170° below its melting point. The emission was constant at this value for an hour but of course decreased gradually over longer periods of time. Life tests were made on some of the better sources. One of them, spodumene, gave considerable emission after 72 percent of the lithium had been emitted as positive ions, and the indication is that 90 percent of the lithium could be evolved as positive ions.

Samples of spodumene and eucryptite examined after ten percent and 40 percent of the lithium had been emitted showed the presence of at least two phases. In each case x-ray diffraction patterns showed some of the original compound. From these results it would seem that the filament remains essentially in equilibrium in the ternary system. This is not unexpected since the temperatures are close to the melting points and any unstable phase that might initially appear as a result of the compound losing lithium ions would tend to come to equilibrium during the time of the experiment.

The work function was determined for some of the better sources and gave the value of about 4 volts which within the limit of error was the same for all compounds tested. The work function decreased slowly with time, and Fig. 1 shows a typical curve for β-eucryptite which, when 60 percent of the lithium was emitted, gave a value for the work function of about 2.70 volts.

The ease with which these compounds emitted positive ions indicated that perhaps a clue to the mechanism of the ion emission could be found in

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[4] This section is the result of some work done by one of us in collaboration with Dr. S. B. Hendricks, Phys. Rev. **44**, 322 (1933).

[5] Hundley, Phys. Rev. **30**, 864 (1927).

[6] Ballo and Ditler, Zeits. f. anorg. chemie **76**, 39 (1912); Jaeger and Van Klooster, Proc. Am. Acad. **16**, 857 (1914); **17**, 239 (1914); **17**, 251 (1914).

[7] Jones, Phys. Rev. **44**, 707 (1933).

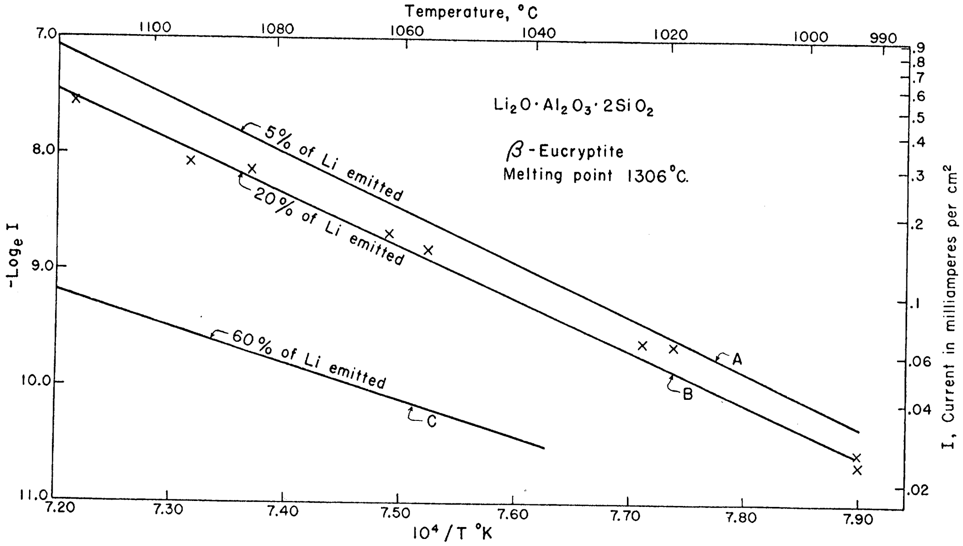

FIG. 1. Thermionic analysis of β-eucryptite. The crosses are the experimental points for curve *B*, showing the typical spread of observed points.

their crystal structures. These structures are not well known but rather probably are three dimensional networks of aluminum-oxygen-silicon ions and possess large "holes" in which the alkali ion is situated; the coordination number of the ion being probably 6 to 8. The alkali ion is therefore comparatively free to migrate within this lattice, and with the aid of small electrolytic potentials which are bound to be present it migrates to the surface and is emitted easily as indicated by the low work function. In order for the lattice to remain neutral, negative charges must leave the lattice also; reversal of potential did not yield any negative current, and the supposition is that the oxygen ions give up their electrons to the platinum strip and escape as neutral molecules. The amount of lithium emitted as positive ions precluded the possibility of any appreciable vaporization of it in any other forms (lithium atoms, LiO molecules, etc.) from the filament.

In preparing any of the other alkali ion sources one is handicapped by the lack of information concerning the ternary systems involved with the exception of the $Na_2O \cdot Al_2O_3 \cdot SiO_2$ system which has been completed. As an empirical rule, however, one can prepare the eucryptite analog of the particular alkali, i.e., $1\ R_2O:1\ Al_2O_3:2\ SiO_2$ and enrich it with R_2O to the point where the enhancement of the emission ceases. A potassium ion source was prepared with the composition $3\ K_2O:1\ Al_2O_3:3\ SiO_2$ which proved to be quite satisfactory though no attempt was made to determine the composition having optimum emissivity.

Table I shows the composition of the various compounds prepared and tested, and are given in the order of decreasing emissivity.

Mass-spectrograph analyses were made of the emission from the $1\ R_2O:1\ Al_2O_3:2\ SiO_2$ sources of all five alkali metals, and the synthetic sources were found to give an emission of ions of the desired element free from more than one or two percent impurity of the other alkalies. They are thus considerably superior to the natural minerals (spodumene, jadeite, leucite, pollucite) which have been widely used as alkali ion sources and whose emissions are frequently found to include ten percent or more of ions of the other alkalies. Presumably the purity of the ion emission is simply a function of the purity of the chemicals employed.

TABLE I. *Emissivity of the various lithium compounds.*

Li_2O	Al_2O_3	SiO_2
1	1	2 Eucryptite
1	1	4 Spodumene
1	1	6
2	1	5
3	1	3
1	0.12	1.6
1	0	1

SOURCES OF OTHER IONS

For the production of ions of other elements than the alkalies, the oxides of the metals in question were chosen as a rule because of their stability and high melting points. Other compounds which were tried often evaporated or decomposed before temperatures high enough for ion emission were reached.

The oxides were coated on helical spiral filaments of 5-mil tungsten wire, using only water as a binder. Strontium and barium oxides, however, attacked the tungsten at comparatively low temperatures and the filaments burned out below 1500°C. This difficulty was overcome by coating the tungsten filament with a thin layer of platinum. Liquid platinum chloride was painted on the tungsten and then burned off with a Bunsen flame. This technique was used in all subsequent work.

The results obtained for the various elements were as follows:

Magnesium

Magnesium ion currents of the order of 10^{-8} amp. were drawn from a filament coated with MgO when the filament was raised to a white heat. A set of observations of the Mg isotopes is plotted in Fig. 2. Peaks also appeared at masses 23 and 27, the mass 23 peak being due to the sodium impurity which appeared in all filaments, and 27 probably belonging to an aluminum impurity.

Calcium

Fig. 2 also shows the isotopes of calcium observed when CaO was heated to a white heat. The potassium peaks at 39 and 41 always appeared but seemed to become smaller with continued running. However, they never became sufficiently small to make possible a thorough search for Ca^{41}. The ratio of the heights of the potassium to the calcium peaks could be adjusted at will by varying the filament temperature. Andradite and grossularite, natural minerals which contain calcium, were heated to see whether they might serve as copious ion sources, but the potassium impurity peaks were so large as to obscure the whole range.

Strontium

Strontium ion currents of 10^{-8} amp. or more were drawn from a SrO coated filament. A peak was observed at mass 84 which we believe to be due to a new isotope. The evidence supporting this hypothesis has already been presented in the *Physical Review*.[8] A small impurity of rubidium appeared in one sample, but was not present when especially pure strontium oxide was used.

Barium

Barium oxide behaved in much the same manner as strontium oxide, and a peak was observed at mass 134 in addition to the peaks corresponding to the known isotopes. This is believed to be due to a new isotope of barium as reported in the reference above.[8]

A search over the negative ion range was made for both the strontium and barium sources and a small peak was detected in both cases at mass 32. This peak has been observed by Barton,[9] who

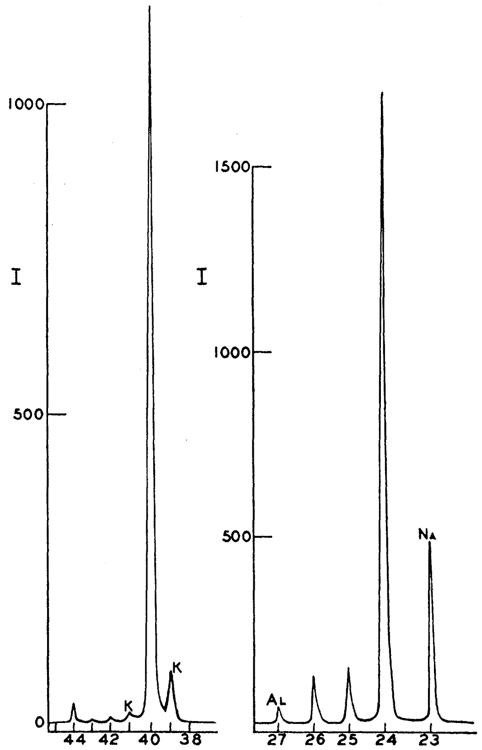

FIG. 2. Mass-spectrograph analysis of emission from magnesium and calcium filament sources.

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[8] Blewett and Sampson, Phys. Rev. **49**, 778 (1936).

[9] Barton, Phys. Rev. **26**, 360 (1925).

suggests that it is due to O_2^-. It was of the order of 1/100 of the size of the positive ion peaks and increased very little in height as the filament temperature was raised.

Aluminum

Aluminum ions were obtained in large quantities from Al_2O_3. The emission began to be appreciable for a filament temperature of about 1400°C and increased to almost a microamp. at about 1600°C. A search over the negative ion range revealed only one peak, at mass 27, appearing at the same temperature as did the Al^+ peak. It is difficult to account for this peak unless it is assumed that it is due to Al^-. Its height varied relative to the positive ion peak, but in general it was of the order of 1/100 as high as the Al^+ peak. Attempts at measurements of work function for the two peaks indicated work functions of the same order of magnitude for the two types of emission. It should be noted also that a search for negative ions from the magnesium ion source which had shown a mass 27 impurity revealed only one negative ion peak, which appeared at mass 27.

Gallium[10]

Ga_2O_3 proved a much weaker source of ions, but at temperatures in excess of 1800°C sufficiently high ion currents were obtained to show up the known isotopes of gallium.

Indium

In_2O_3 was the most copious ion emitter observed, with the exception of the alkalies. Indium ions came off in large quantities at very low temperatures, the ion emission becoming appreciable around 900°C and increasing rapidly to be of the order of microamps. An isotopic analysis of indium has been reported[8] and curves are given in a forthcoming paper by Sampson.[11] The negative ion emission due to Al_2O_3 inspired a search for negative indium ions, but none was observed.

Other elements

Ion currents of the order of 10^{-10} amp. were drawn from oxides of Ti, V, Mn, Y, and Ce, but the emission was very unsteady and was thoroughly unsuited to use with mass spectrographs which employ electrical detection.

No ions except those of alkali impurities could be detected from SiO_2, BeO, beryl, Er_2NO_3, ZrO_2 or B_6C although the filaments carrying these salts were heated to about 2500°C. ZnO refused to stay on a filament above about 1400°C. Filaments carrying $Fe_2(NO_3)_3$ and Cr_2O_3 burned out at low temperatures in spite of the platinizing process.

At no time were any ions observed with double or multiple charges.

Discussion

Although no exact mechanism for the emission of positive ions from compounds is indicated in the present work, in general the following requirements seem necessary in order that emission take place: (1) that the lattice be an ionic one; (2) that the forces holding the ion in the lattice be small, as in the alkali alumino-silicates; or if the forces are not small, that the compound be stable thermally so that sufficient energy can be supplied to the lattice to effect a partial breakdown of the structure which will permit singly charged ions to escape with the aid of the drawing-out potential. This seems to be the case with MgO, CaO, BaO, Al_2O_3, In_2O_3, and Ga_2O_3.

Another viewpoint is suggested by the results of a number of workers[12] on thermionic emission of electrons from alkaline earth oxides. These observations seem to indicate that under the influence of the drawing-out potential an electrolysis of the crystalline oxide takes place. The metallic ions would be brought to the surface to evaporate partly as atoms and partly as ions. Studies (see the texts given in reference 1) of ionization of alkali vapors by hot filaments suggest that if the work function of the surface is greater than the ionization potential of the metal, all of the metal will evaporate in the ionized state.

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[10] We are indebted to Mr. M. B. Sampson for the observations here reported on gallium.

[11] Sampson and Bleakney, Phys. Rev., this issue.

[12] Cf. Becker, Phys. Rev. **34**, 1323 (1929); Becker and Sears, Phys. Rev. **38**, 2193 (1931).