CHARACTERISTIC X-RAYS FROM LITHIUM

By Gerhard K. Rollefson

Abstract

Critical potentials for metallic lithium, determined photo-electrically.—A previously described method[1] has been used to determine radiation and ionization potentials of metallic lithium. The values obtained are 39.2, 43.07, and 46.0 volts as radiation potentials and 48.4 volts as the ionization potential. In terms of energy levels these are interpreted as corresponding to the differences $1_1 \rightarrow 2_1$, $1_1 \rightarrow 2_2$, $1_1 \rightarrow 3_1$, and $1_1 \rightarrow \infty$ respectively.

Kα lines of light elements.—The radiation potential at 43.07 volts corresponds to the Kα line of lithium. This value is used to extend the Moseley curve for the Kα lines, and the values for the other light elements are obtained by interpolation. The wave-lengths in angstrom units given for these elements are: Li, 286.5; Be, 132.8; B, 74.4; C, 49.0; N, 33.2; O, 24.4; F, 18.6; Ne, 14.8.

IN a previous paper[1] a method has been described for determining critical potentials of solids. This method has been used to determine the critical potentials corresponding to the x-ray spectrum of lithium.

Experimental Details

The apparatus used was essentially the same as that described previously except that the target was mounted so that it could be water cooled if desired. The target consisted of Kahlbaum's metallic lithium mounted on a brass base. In order to have a clean surface of metal exposed to the electron bombardment the coating of oxide and nitride was scraped off and the surface dipped in liquid naphthalene which solidified to form a protecting coating which could be pumped off after the target had been sealed into the tube. The tube was thoroughly baked and evacuated so that the pressure never exceeded 10^{-5} mm while readings were being taken and was usually considerably lower.

The intensity of the radiation from the lithium was so low that after a few runs the effect of the strong general radiation from the thin film of tungsten which distilled from the filament on to the target became sufficient to obliterate the breaks due to the excitation of characteristic lithium radiation. The disturbing effect of the general radiation of tungsten could not be eliminated entirely since it is necessary to heat the filament for some time before vacuum conditions become sufficiently good to make quantitative measurements. The rate of contamination

[1] Rollefson, Phys. Rev. **23**, 35 (1924)

of the target, however, was materially reduced by using filaments which had been treated with thorium oxide so that they could be operated at a lower temperature.

The experimental procedure followed was essentially the same as that for the low voltage work on iron. The filament was kept at a constant temperature throughout the run so as to maintain the initial conditions in the tube as constant as possible. The accelerating potentials were applied from the negative end of the filament to the target. The potential drop across the filament varied with the filament from 0.8 to 2.0 volts. Larger potential drops could not be used without increasing the interval between readings which would mean a decrease in the accuracy of the work.

Some preliminary measurements were made with a pressure of approximately 10^{-4} mm in the tube soon after starting to heat the filament. Under these conditions accurate measurements could not be obtained but it was possible to get an approximate determination of the voltage range in which the characteristic radiation of lithium is excited, before the effect of the tungsten distilled from the filament became appreciable. These results indicated that with a fresh target, accelerating potentials of less than 40 volts produced practically no radiation capable of giving a photo-electric current from a platinum plate. This is not surprising since the frequencies corresponding to the "optical" series of lithium are less than the threshold frequency of platinum and the general radiation from such a light element is extremely low. Therefore it is to be expected that the photo-electric current would be very small until the x-ray spectrum of lithium is excited.

Accurate measurements were made over the range from 30 to 60 volts. The results show three very reproducible critical potentials and in some cases a fourth one at a higher value. One of the curves obtained is shown in Fig. 1. (The fourth break is quite marked in this case but in some of the other curves it did not show at all.) The absolute values at which the breaks in the curves occurred varied somewhat with the different targets and filaments but the differences between breaks remained constant. The results obtained in one set of four consecutive runs with the same filament and target are given in Table I.

TABLE I

	1	2	3	4
	40.3	44.1	46.9	49.6
	40.1	43.9	46.9	49.1
	40.15	44.2	47.15	49.4
	40.25	44.0	47.1	.....
Averages:	40.2	44.05	47.0	49.4

Since the filament is at a much higher temperature at the center than it is at the ends, most of the bombarding electrons start from a potential more nearly that of the center of the filament than that of the negative end, therefore the values given in the above table should be shifted an amount corresponding to half the total potential drop across the filament. Making this change for the set of runs given in Table I, the values 39.2, 43.05, 46.0, and 48.4 volts are obtained. Due to uncertainty in the initial conditions the absolute values of these critical potentials may be in doubt as much as half a volt. The values for the differences were found to be $3.87 \pm .15$ volts between 1 and 2, and $2.95 \pm .15$ volts between 2 and 3.

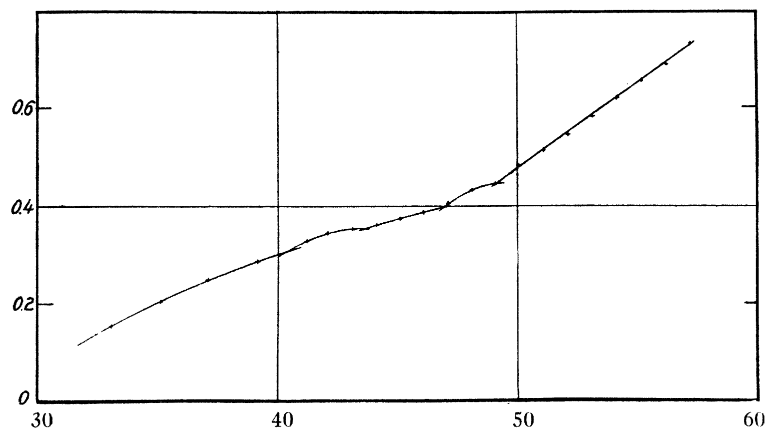

Fig. 1. Photo-current as a function of accelerating voltage.

There are two other corrections that must be considered in this work. K. T. Compton has pointed out that the true critical potential is represented by the potential through which the electron falls in going from the filament to the target plus the work function of the target. The effect of the work function of the target has been neglected in earlier work but it is apparent that it must be considered in order to determine the total energy possessed by the electron at the time it excites an atom in the target. The work function of lithium may be obtained from Millikan's value for the photo-electric threshold[2] or the long wave-length limit 5263A which corresponds to 2.34 volts for the work function.

The other correction to be made is that for the contact potential between the filament and the target. The tube was not arranged so that this could be determined directly but an approximate value may be calculated from the values for the work functions of tungsten and lithium.

[2] Millikan, Phys. Rev. **18,** 236 (1921)

For tungsten Davisson and Germer[3] give 4.50 volts. The difference is 2.16 volts and is a retarding potential for electrons going from the tungsten to the lithium. As this is opposite in sign to the other correction and is equal in magnitude to it within the limits of the experimental errors involved in their determinations, therefore the two cancel each other and we may take as the final corrected values 39.2, 43.07, 46.0, and 48.4 volts.

Discussion of Results

According to the Bohr theory the neutral lithium atom consists of a nucleus with three positive charges, two electrons in 1_1 orbits, and one electron in a 2_1 orbit (Bohr notation used). The energy states to which the 2_1 electron may be resonated have been determined by a study of the arc spectrum of lithium. The energy necessary for the complete removal of this electron is 5.33 volts. If lithium is bombarded by electrons with greater energy no new characteristic radiation can be excited until the energy of the bombarding electrons becomes sufficient to raise one of the 1_1 electrons to an orbit of higher quantum number. If the electron is raised to the 2_1 level it is to be noted that characteristic radiation can not be produced by the direct return of this electron to the 1_1 level since such a transition is prohibited by the selection principle. In such a case the atom must return to its normal state in some other way. One possibility is that one of the electrons in the 2_1 level of the excited atom may be raised to the 2_2 or some higher level, either by absorption of radiation or by a second electron impact, and then drop back to the 1_1 level. Another possibility is that a free electron from the metal or one of the bombarding electrons may fall directly to the 1_1 level, one of the 2_1 electrons being released at the same time. Either of these processes would produce a new type of radiation; therefore any study of critical potentials of lithium by the photo-electric method might be expected to show a critical potential corresponding to the $1_1 \rightarrow 2_1$ transition although the radiation actually produced would have a frequency corresponding to a greater energy difference. If the electron is resonated to a higher level than the 2_1 it can return to the 1_1 either directly or in two or more steps without the aid of an outside agency.

Considering the results which have been obtained the most natural assumption to make is that the first critical potential observed corresponds to the transfer of an electron from the 1_1 to the 2_1 level, and the second to a transfer from the 1_1 to the 2_2. If this is the case the difference

[3] Davisson and Germer, Phys. Rev. **20**, 300 (1922)

between the two is equal to the energy necessary to change the atom from a condition in which it has one electron in the 1_1 level and two in the 2_1 to a condition in which it has one in each of the 1_1, 2_1, and 2_2 levels. This value should be comparable to the differences between the 2_1 and 2_2 levels in other atoms in which the field of force in the vicinity of the two quantum orbits is approximately the same as in the excited lithium atom. One system of that type is the beryllium atom. Some of the term values for beryllium have been calculated by Birge;[4] he gives the 2_1 to 2_2 difference as 3.44 volts. Another system of this type is Li^+ for which Schüler[5] has found the 2_1 to 2_2 difference to be 4.2 volts. The presence of another electron in the 2_1 level would decrease this difference somewhat, therefore the value 3.87 volts, observed in these experiments, is about what might be expected for the type of change postulated above.

The third critical potential may correspond to resonance to one of the three quantum orbits. For beryllium Birge gives 6.9 volts as the difference between the 2_1 and 3_1 levels. The observed difference between the first and third breaks in the curves for lithium is 6.8 volts, hence the third break is attributed to resonance from the 1_1 to the 3_1 level. The higher levels are too close together to be resolved by the apparatus used in these experiments, therefore the fourth break probably represents ionization rather than resonance. As a check on this hypothesis we may again refer to Birge's values for beryllium. He gives 9.9 volts as the ionization potential, which is in fair agreement with the difference of 9.2 volts between the first and fourth breaks obtained for lithium. To summarize, the four observed critical potentials are interpreted as follows: 39.2 volts ($1_1 \rightarrow 2_1$), 43.07 volts ($1_1 \rightarrow 2_2$), 46.0 volts ($1_1 \rightarrow 3_1$), and 48.4 volts ($1_1 \rightarrow \infty$).

According to this interpretation the break at 43.07 volts corresponds to the $K\alpha$ line of lithium and thus supplies a point for use in the extension of the Mosely curve for the $K\alpha$ lines. Another point which may be used in this connection is the value for the $K\alpha$ of carbon obtained by Lukirsky[6] using a different method from the one described in this paper. His value is $\lambda = 48.9$A, $\nu/R = 18.60$. The curve using these values for lithium and carbon, Hjalmar's[7] values for the elements from sodium to chlorine, the first Lyman line of hydrogen, and the $1S-2P$ line of helium, is shown in Fig. 2. It is to be noted that the line apparently continues perfectly straight down to lithium, only helium and hydrogen being off

[4] Birge, J. Opt. Soc. Amer. and R. S. I. **8**, 233 (1924)
[5] Schüler, Naturwissenschaften **12**, 579 (1924)
[6] Lukirsky, Phil. Mag. **47**, 466 (1924)
[7] Hjalmar, Zeits. f. Physik **1**, 439 (1920)

this line. This curve may be used to obtain the values of the Kα lines of the intervening elements by interpolation. These interpolated values together with the observed values for carbon and lithium are given in Table II.

TABLE II

Kα lines of light elements

Atomic number	Element	Critical potential	ν/R	Wave-length
3	lithium	43.07 volts	3.18	286.5A
4	beryllium	93.0	6.86	132.8
5	boron	166	12.25	74.4
6	carbon	252	18.60	49.0
7	nitrogen	372	27.46	33.2
8	oxygen	507	37.45	24.4
9	fluorine	664	49.00	18.6
10	neon	835	61.77	14.8

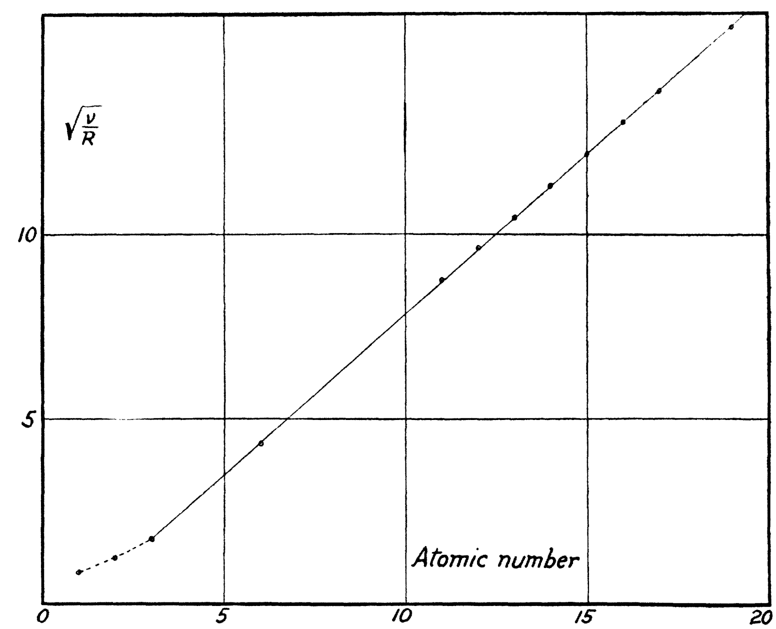

Fig. 2. Moseley curve for Kα lines of light elements.

Other investigations concerning the excitation of the K electrons of lithium have been carried on by Mohler,[8] Holtsmark,[9] and McLennan and Clark.[10] Mohler, studying the low voltage arc spectrum of lithium, found that a line due to Li^+ appeared in a long exposure at 45 volts.[11]

[8] Mohler, Science **58,** 468 (1923)

[9] Holtsmark, Phys. Zeits. **24,** 225 (1923)

[10] McLennan and Clark, Proc. Roy. Soc. A **102,** 389 (1923)

[11] For the classification of the lines due to Li^+ see Schüler, loc. cit.[5]

This line could not appear before the arc voltage became high enough to resonate a 1_1 electron, therefore, this experiment shows that the resonance potential lies below 45 volts. McLennan and Clark found three critical potentials at 13, 31.8, and 37 volts but their published curves are so radically different from those obtained by other investigators in this field that it is quite likely that there were disturbing influences in their tube which materially affected the results. The work by Holtsmark was done with lithium in the combined state. He took readings at five volts intervals and therefore failed to find any resonance points, observing only the general rise of the curve after passing ionization. His value for the ionization of the 1_1 level is 52.6 volts (two published values are 52 and 54 volts). This is somewhat higher than the value obtained by the writer for metallic lithium as might be expected since in the compound the lithium atom has "lost" its valence electron to some other atom. If this electron were completely removed from the system the ionization potential of the 1_1 level would be increased about 9 volts. Actually the electron is only slightly displaced so that the observed effect should be considerably smaller. This probably is the principal reason for the difference between Holtsmark's value and that given in this paper.*

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* Note added April 30, 1925.—Since the above was written a direct determination of the $K\alpha$ line of fluorine has been published by Bäcklin, Siegbahn, and Thoraeus (Phil. Mag. **49**, 513, 1925). Their value of 18.37A is in good agreement with the interpolated value 18.6A given in this paper.

Another determination of the K limit of lithium, using lithium fluoride as a target, was published recently by Miss Levi (Trans. Roy. Soc., Canada **18**, III, 159, 1924). Her value of 47 volts agrees fairly well with that given in this paper, in fact Fig. 3 of her paper actually shows the break at 48 volts. She also gives three lower excitation limits at 8.4, 16.9, and 24.3 volts interpreting them as corresponding to the energy necessary to remove the L electron from one, two, and three atoms. The energy necessary to remove the L electron from lithium is known quite accurately from ordinary spectroscopic data and is 5.368 volts, hence the lower limits observed by Miss Levi are probably not due to lithium but to the fluoride ion which was present in the target.