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Charge Transfer Between Li Ions and Li Atoms in the 14–1000-eV Energy Region*

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By means of a crossed-beam technique, the absolute cross section for charge transfer between lithium ions and lithium atoms has been measured for incident ion energies ranging from 14 to 1000 eV. The lithium ions are produced thermally in a β-eucryptite source and are accelerated and focused into a ribbon beam in a Pierce gun. The total energy spread of the beam is less than 3% at all energies; mass analysis shows that above 1000°C emitter temperature the impurity ions in the beam are below 0.2%. This ion beam traverses a high-density, collimated lithium vapor beam issuing from an oven. A typical density of neutral lithium atoms in the interaction region is 10^{13} atoms/cm³. The slow ions produced in the charge-transfer interaction are collected on a negatively biased cage surrounding the interaction volume of the two beams. The slow-ion charge-transfer current completely accounts for the ion-beam attenuation, thus indicating that all scattered beam ions are collected. The vapor-beam density was determined by condensing the vapor on a cold target, dissolving the metallic lithium thus collected, and titrating the resulting solution. The cross section for charge transfer varies from 240×10^{-16} cm² at 14 eV incident ion energy to 80×10^{-16} cm² at 1000 eV, and has the expected energy dependence for resonant charge transfer

$$Q^{1/2} = 19.3\times10^{-8} - 3.5\times10^{-8} \log E,$$

where the incident ion energy E is in eV and Q is in cm².

INTRODUCTION

THE resonant charge transfer reaction of the type

$$X^+ \text{ (fast)} + X \text{ (slow)} \rightarrow X \text{ (fast)} + X^+ \text{ (slow)}$$

(where X represents any atom or molecule) has been investigated for many atomic systems.[1] This reaction is of interest for two reasons: (i) it is somewhat easier to treat theoretically than most interactions involving complex atomic systems, and (ii) the unusually large cross sections at low relative velocities make resonant charge transfer important in a number of applications. The alkali metals have received particular attention because of their potential use in such applications as ion propulsion, ionization in high-temperature gases, etc. Recent measurements, as well as a review of earlier results for the case of Cs$^+$ in Cs gas, have appeared in

a paper by Marino et al.[2] Only scattered measurements of resonant charge transfer are available for the other alkalis. In this paper we present results of a measurement of the absolute charge transfer cross section for the reaction Li$^+$+Li → Li+Li$^+$ for incident ion energies from 14 to 1000 eV.

EXPERIMENTAL DETAILS

The general layout of this crossed beam experiment is shown in Fig. 1.

Ion Source

Rather intense and pure alkali-ion beams are readily obtainable from thermal emitters. Surfaces coated with alkali aluminosilicates can be used as ion sources which yield current densities of mA/cm² when heated to sufficiently high temperatures.[3] Since the ions are emitted thermally, the energy spread of the ions leaving the

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[1] O. Heinz and E. J. Feinler, Stanford Research Institute, Project SU 2853, Interim Technical Report No. 1, 1961 (unpublished).

[2] L. L. Marino, A. C. H. Smith, and E. Caplinger, Phys. Rev. **128**, 2243 (1962).

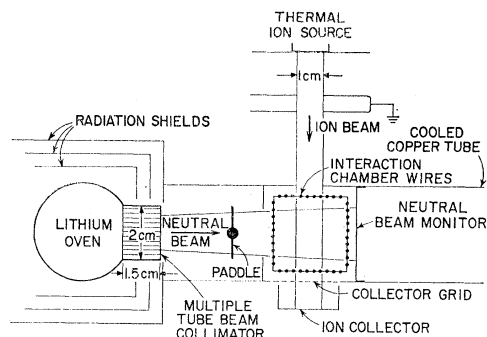[3] G. Couchet, Ann. Phys. (Paris) **9**, 731 (1954).

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Fig. 1. Schematic drawing of the apparatus.

source is on the order of 0.1 eV and if a properly shaped accelerating field is used final ion beams with an energy spread of only a few tenths of an eV can be obtained for any beam energy above 1 or 2 eV.[4] The most commonly used material for Li ion sources is lithium aluminosilicate ($Li_2O.Al_2O_3.2SiO_2$) also known as the mineral β-eucryptite.[5,6] When heated to temperatures of 1000°C
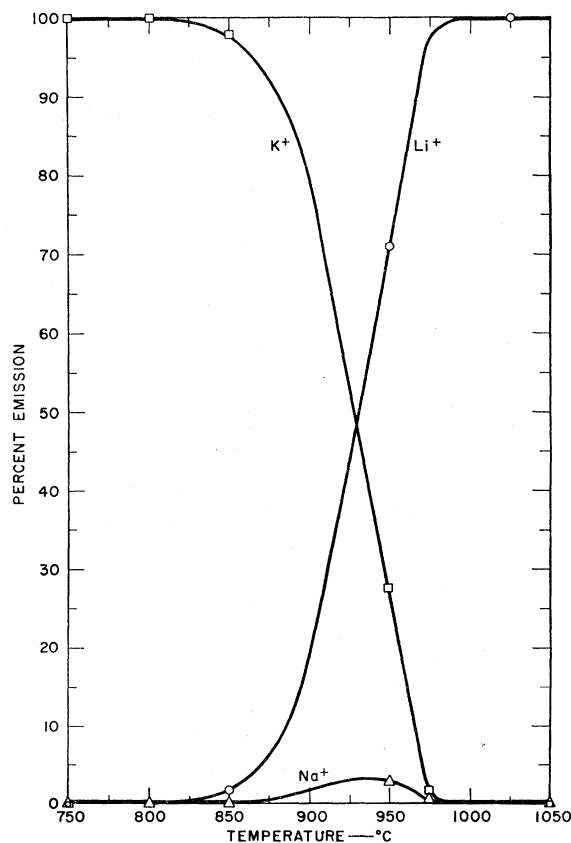
Fig. 2. Mass analysis of the ion source emission.

or more this material emits predominantly Li ions. For our particular sample, magnetic mass analysis of the beam showed less than 0.2% impurity ions above 1000°C (see Fig. 2). The β-eucryptite was prepared from natural lithium carbonate (Li_2CO_3), alumina (Al_2O_3), and silica (SiO_2) as described by Allison and Kamegai[5] and Waldron.[7] It was applied as a suspension in amyl acetate (containing a little "parlodion") to the scored front surface of a tantalum boat as shown in Fig. 3. The dimensions of the emitter surface are 1.5×1 cm. A tungsten wire grid spot-welded to the boat assisted adhesion of the coating and served to maintain the β-eucryptite surface at the same potential and temperature as the boat.

The boat was heated by 0.007-in. tungsten filament wound through alumina tubing and embedded in Alundum cement. Heat losses were minimized by two nickel radiation shields.
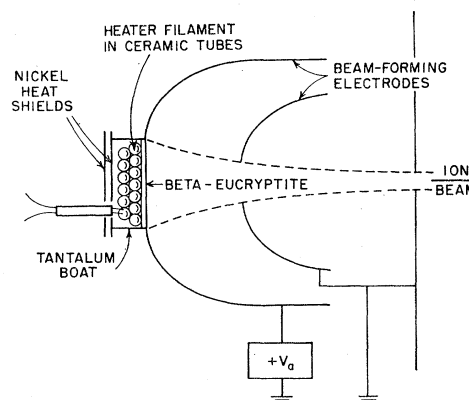
Fig. 3. Lithium ion source.

The ion gun shown in Fig. 3, consists of the emitter described above and accelerating electrodes mounted on a Lavite holder designed to provide adjustment of the source parameters. The electrode geometry was based on the Pierce principle[8,9] and followed a design by von Ardenne.[10]

The surface temperature of the β-eucryptite was determined with an optical pyrometer. The first ion emission (K^+) was observed at a power input to the filament of 15 W corresponding to a temperature of 600°C. At 1000°C and a heater power of 70 W the beam was almost entirely Li^+ (see Fig. 2). At these temperatures the lifetime of the source was governed by heater failure which usually occurred after a few tens of hours of operation, and appeared to result from some reaction of the

[4] W. W. Lambert, MS thesis, U. S. Naval Postgraduate School, 1963 (unpublished).
[5] S. K. Allison and M. Kamegai, Rev. Sci. Instr. 32, 1090 (1961).
[6] F. M. Johnson, RCA Rev. 22, 427 (1962).

[7] J. C. Waldron, United Kingdom Atomic Energy Authority, Research Group Memorandum AERE-M952, 1962 (unpublished).
[8] O. Klemperer, Electron Optics (Cambridge University Press, London, 1953), p. 269.
[9] J. R. Pierce, Theory and Design of Electron Beams (D. Van Nostrand Company, Inc., New York, 1954).
[10] M. von Ardenne, Tabellen der Elektronenphysik, Ionenphysik Und Ubermikroskopie (Deutscher Verlag der Wissenschaften, Berlin, 1956), Band I, pp. 507–519.
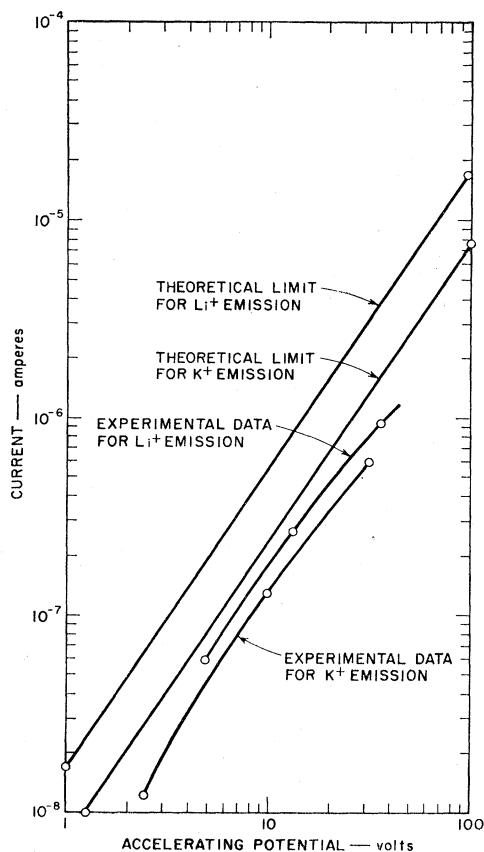
F𝐼G. 4. Ion source emission as a function of accelerating potential.

tungsten with the Alundum cement. This lifetime was about an order of magnitude less than the calculated lifetime due to lithium exhaustion in the β-eucryptite.

For the geometry of our source and an emitter area of 1.5 cm^2 substitution of the appropriate parameters in the equations given by von Ardenne[10] predict the following maximum beam currents for Li$^+$ and K$^+$

$$I_{K^+} = 0.53 \times 10^{-8} V_a^{3/2} \text{ A}$$
$$I_{Li^+} = 1.7 \times 10^{-8} V_a^{3/2} \text{ A},$$

where V_a is the accelerating potential in volts. These curves and the corresponding experimental results are shown in Fig. 4. It is seen that the source can produce beams close to the theoretical space charge limit.

Lithium-Vapor Beam Oven

To study charge transfer between lithium ions and atoms an appropriate target of lithium atoms must be provided for the lithium ion beam. This was achieved by directing a collimated lithium-vapor beam issuing from an oven operating at about 700°C across the ion beam and condensing the vapor on a cooled surface beyond the beam interaction region.

The soft-iron cylindrical oven was capped with a

threaded cover using a metal O-ring as a seal. A chromel-alumel thermocouple spot-welded to the cover measured the oven temperature. The heater, wound with 0.015-in. tantalum wire through alumina tubing (to insulate it from the oven) was confined to a side arm, which also contained the collimating system. This position of the heater insured that the collimating system was the hottest part of the oven and thus provided the proper density gradient of lithium vapor for optimum collimation. A triple-wall radiation shield surrounding the oven reduced heat losses so that a power input of 125 W raised the oven temperature above 700°C. The vapor pressure of lithium at 700°C is approximately 0.5 Torr.[11] The collimator presented an area of $2 \times \frac{1}{2}$ cm to the effusing lithium atoms and was 1.5 cm long as indicated in Fig. 1. The collimator was made from alternate layers of plane and corrugated tantalum foil 3×10^{-4} in. thick. The final collimating array resembled a bundle of tubes with a diameter of about 0.020 in. Such an array will operate as a fairly efficient collimator for oven pressures on the order of a few tenths of a Torr.[7] The vapor beam was further collimated by a $2 \times \frac{1}{2}$-cm slit just in front of the interaction region. Between this second collimating slit and the oven a movable paddle could be used to interrupt the vapor beam. After passing through the interaction region, the beam was condensed on a copper shell cooled by a 1-in. copper rod leading to a dry ice-acetone mixture outside the vacuum system.

Thermodynamic calculations indicate that under the specified operating conditions less than 3.5% Li$_2$ should be formed in the interior of our oven.[11]

Lithium-Vapor Beam Flux Measurements

An attempt was made to measure the flux of neutral lithium atoms emerging from the oven by the usual surface ionization method using a tungsten oxide surface.[12] It was found however that at fluxes exceeding 10^{16} atoms/cm^2/sec the response of the detector leveled off and then decreased as the flux was further increased.[13] Since the flux required for the charge-transfer measurements was on the order of 10^{18} atoms/cm^2/sec the surface ionization method was not suitable and an integrating chemical method was devised and used to measure the neutral beam density. All of the lithium passing through the interaction chamber was condensed on a neutral-beam monitor (Fig. 1) consisting of a copper plate with 1-mm-diam copper wires spaced 1 mm apart mounted approximately $\frac{1}{8}$ in. above its surface. When assembled the wires were parallel to the ion beam.

[11] A. N. Nesmeyanov, *Vapor Pressure of the Chemical Elements* (Elsevier Publishing Company, Amsterdam, The Netherlands, 1963).

[12] S. Datz and E. H. Taylor, in *Recent Research in Molecular Beams*, edited by I. Estermann (Academic Press Inc., New York, 1959). E. Ya. Zandberg and N. I. Ionov, Usp. Fiz. Nauk **57**, 581 (1959) [English transl.: Soviet Phys.—Usp. **2**, 255 (1959)].

[13] D. C. Lorents and G. Black, Stanford Research Institute, Project 3857, Technical Report 19, 1964 (unpublished).
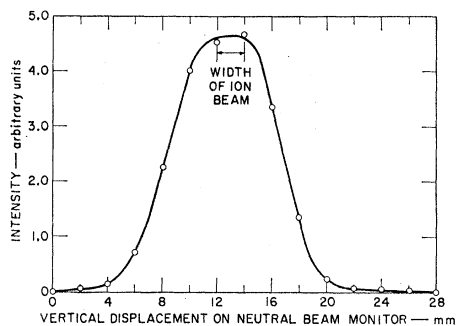
FIG. 5. Neutral-beam profile.

Measurement of the amount of Li condensed on each of the wires and on the plate enabled a profile of the neutral beam as well as the total flux through the interaction chamber to be determined (Fig. 5).

After an experiment the neutral beam monitor was removed from the copper shell. The lithium on each wire and on the plate was dissolved in water using separate flasks. This converted the lithium to lithium hydroxide (any surface nitride on the lithium would be similarly converted). Any ammonia (from the nitride) was removed by boiling and the lithium determined as the hydroxide by titrating with standard acid using phenolphthalein as indicator. The accuracy of this method for determining the amount of lithium deposit was ±3%.

A probe was devised to relate the total flux at the monitor to the lithium concentration in the interaction region. This consisted of a 2-mm-wide strip of 0.020-in.-thick copper (the height of the ion beam was 2 mm). With the ion beam collector and its grid removed, the probe was inserted along the center of the interaction region in the direction of motion of the ion beam. By measuring the Li flux using both the probe and the beam monitor for a given time interval, the monitor was calibrated in terms of the average flux at the center of the interaction region.

Measurements with the probe in position showed that an average lithium flux of 4×10^{17} atoms/cm²/sec over the $1\frac{1}{2}$ in. width of the interaction chamber was produced at an oven temperature of about 700°C. This would indicate a flux $> 10^{18}$ atoms/cm²/sec at the center of the vapor beam. However, for the calculation of the cross section only the integrated value of the vapor-beam density is necessary. To calculate the volume density of Li atoms in the interaction region from the flux measured by the probe the average gas velocity $\langle v \rangle$ corresponding to a temperature of 700°C was used.

Interaction Region

The volume of intersection of the ion and vapor beams is surrounded by a cage consisting of a pair of tantalum plates mounted above and below the beams and connected by fine vertical grid wires. Slow charge-transfer ions created in the interaction volume are collected on the cage by biasing it a few volts negative. The grid wires intercept about 2% of the ion beam as it traverses the cage. Since the Li vapor beam monitor was calibrated with the cage in place, interception of Li by the wires was accounted for.

The ion beam was defined by two 1×0.2-cm slits mounted 5 cm apart. The second of these slits was mounted on the copper shell surrounding the interaction volume. After traversing the interaction volume the ion beam was collected in a 2×1-cm Faraday cup. The size of the cup insured that the ion beam was not attenuated appreciably by scattering. A grid in front of the cup, negatively biased, suppressed any secondary electron emission from the cup.

MEASUREMENT PROCEDURE AND RESULTS

The oven was charged with 2 to 3 g of lithium in an argon-filled dry box. Before removal from the box, the lithium was covered with benzene to reduce the chemical reaction with the atmosphere during assembly of the apparatus. Before any measurements were performed, the oven and ion source were outgassed by raising the oven temperature to about 250°C for 12 h and the ion source to 1000°C for 2 h. During this procedure the paddle was inserted into the vapor beam to block passage of the atoms into the interaction region.

With the paddle still intercepting the vapor beam the oven temperature was gradually raised to the operating value of 700°C. The desired accelerating potential was applied to the ion source, thus providing a Li⁺ beam flowing through the interaction region to the ion collector (Fig. 1). With the oven temperature stabilized, the paddle was raised to allow the thermal lithium beam to intersect the ion beam in the center of the interaction chamber.

The chamber was biased negatively to collect the slow ions resulting from charge exchange when the two beams intersected. The amount of bias required was determined by increasing the negative potential on the chamber until the slow ion current became saturated. Raising the paddle gave rise to an increase in the current to the interaction chamber and an attenuation of the ion-collector current. These two signals, found to agree within experimental error, indicated that the ion beam attenuation was due only to charge transfer and did not include a contribution from scattering.

For a constant vapor beam, the relative charge-transfer cross section was directly obtained from a measurement of the fast-ion beam current and the current of slow ions collected by the interaction chamber. These measurements were carried out for incident-ion energies ranging from 14 to 1000 eV.

Next, measurements were performed at one energy to determine the absolute cross section. The ion source and oven were allowed to stabilize for a time before starting the measurement to insure constant beams for

the run. With the incident ion energy fixed at 100 eV and -15 V on the interaction chamber (that is, for 115 eV ions passing through the interaction chamber), the charge-transfer current was monitored for a fixed time (say, 30 min) at this one energy. To obtain an absolute value of the charge-transfer cross section the number density of Li atoms in the interaction region must also be known. It is well known that the measured flux density f(atoms/cm²/sec) and the number density n(atoms/cm³) in the vapor beam obey the relation

$$n = f/\langle v \rangle,$$

where $\langle v \rangle$ is the mean speed of Li atoms in the oven.[14] However, for the calculation of the charge-transfer cross section, only the total target "thickness"

$$n_T = \int_0^l n(x)dx$$

along the ion-beam path is needed. This can be obtained directly from the amount of Li deposited on the appropriate wires (see Fig. 5).

The cross section can now be obtained in the usual fashion, since for our experimental conditions the primary ion beam is given by $I = I_0 e^{-n_T Q}$ and the charge-transfer current $i = I_0 - I$ as indicated above. Thus

$$i = I_0(1 - e^{-n_T Q}) \quad \text{and} \quad Q = -\frac{\ln(1 - i/I_0)}{n_T},$$

where Q = total charge-transfer cross section (cm²), i = charge-transfer current (slow ions) (A), I_0 = initial
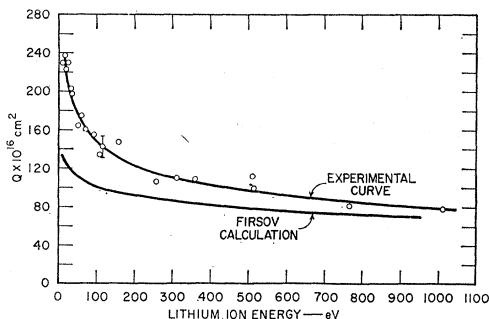

FIG. 6. Charge transfer cross sections for Li⁺ in Li.

[14] N. F. Ramsey, *Molecular Beams* (Oxford University Press, London, 1956).

Li⁺ beam (A), and n_T = target thickness (atoms/cm²). These measurements established the absolute cross section at 115 eV as $(143 \pm 11) \times 10^{-16}$ cm². The relative data obtained earlier were then normalized to this point. The variation of the cross section with incident ion energy obtained in this manner is shown in Fig. 6.

The random error in the determination of the cross section at 115 eV was about $\pm 6\%$ which is within the estimated experimental error of $\pm 8\%$. The formation of the dimer Li₂ in the oven could lead to a value of the cross section too low by as much as 7% assuming no charge transfer of Li⁺ in Li₂. However, the error is believed to be less than that due to the breakup of the dimers in the collimating tubes.

DISCUSSION

Although a number of measurements of resonant charge transfer for the alkali atoms exist[1,2] we are not aware of any previous measurements for the Li⁺—Li system.

Of the several theoretical models which have been proposed the one most widely used is Firsov's.[15] The curve of charge-transfer cross section as a function of energy using Firsov's formula was calculated for Li ions in Li and the results are shown in Fig. 6 for comparison with the experimental curve. The fact that the experimental curve lies somewhat higher than the theoretical is also true for cesium.[2] The shape of both the theoretical and experimental curves can be represented[16] by

$$Q^{1/2} = a - b \log E,$$

where E is the ion energy. The best fit of the experimental curve to the above formula yields the following expression for the charge-transfer cross section as a function of ion energy:

$$Q^{1/2}_{(Li^+/Li)} = 19.3 \times 10^{-8} - 3.5 \times 10^{-8} \log E,$$

where Q is in cm² and E is expressed in eV.[17]

ACKNOWLEDGMENT

The authors wish to acknowledge the capable help of R. Leon during all phases of the experimental program.

[15] O. B. Firsov, Zh. Eksperim. i Teor. Fiz. **21**, 1001 (1951).

[16] A. Dalgarno, *The Threshold of Space*, edited by M. Zelikoff (Pergamon Press, Ltd., London, 1957), p. 186.

[17] An incorrect value for this cross section was reported in Bull. Am. Phys. Soc. **9**, 426 (1964). An erratum giving the correct value was published in Bull. Am. Phys. Soc. **9**, 606 (1964).