

Characteristic Electron Energy Losses in Sodium and Potassium*

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(Received 14 February 1964; revised manuscript received 8 April 1964)

The characteristic electron energy-loss spectra of sodium and potassium have been obtained with improved resolution. Each spectrum was found to exhibit normal surface and volume plasma-oscillation loss peaks; the anomalies reported previously were not observed. Intrinsic surface and volume energy losses of 3.82 ± 0.10 eV and 5.85 ± 0.05 eV in sodium, and 2.75 ± 0.10 eV and 4.05 ± 0.15 eV in potassium, are reported.

INTRODUCTION

ANOMALOUS energy losses have been reported for the first volume plasmon peaks observed in the characteristic loss spectra of both sodium and potassium.¹ The reported departure of the energy loss corresponding to the first volume-loss peak from the mean of the differences between succeeding peaks is quite unexpected, and does not find an explanation in the theoretical treatment of plasma oscillations.²⁻⁴

Measurements in greater detail of the spectra of these elements were planned, using the same energy spectrometer as previously. The resolution and accuracy of the observations were improved by making modifications in the spectrum-scanning and data-recording equipment.

APPARATUS AND EXPERIMENTAL PROCEDURE

The spectrometer and electron gun employed in the present studies were the same as those described earlier.⁵ Primary monoenergetic electrons from the gun were incident upon the target; the energy spectrum of those electrons which passed through the entrance slit system of the spectrometer after having been scattered through 90° in the proximity of the target surface was analyzed by means of a 127° electrostatic energy analyzer. As before, the target material was evaporated in vacuum on to a tantalum base to produce the target itself; evaporation was carried out continuously during a run, which might last for up to an hour, in order to ensure the maintenance of a clean surface. That the surface presented to the beam from the electron gun indeed remained unchanged was subject to frequent check, as described below. The target, which was enclosed almost completely by a cold-trap cooled with liquid nitrogen, was not intentionally cooled and its temperature was observed to fall below room temperature by not more than a few degrees Centigrade, as measured by a thermocouple.

Considerable improvement in stability and repro-

ducibility was achieved by installing new high-voltage supplies⁶ for the electron gun and energy analyzer. The consequent reduction in ripple resulted in a slight reduction in the width of each peak and thus improved the energy resolution of the system.

Also prior to the current series of observations a major change was made in the method of recording spectra. Electrons focused at the exit slit of the analyzer, having an energy determined by the instantaneous value of the deflector-plate potential difference, were detected by an electron multiplier as before. The potential difference applied between the deflector plates of the analyzer, symmetrically positive and negative with respect to the entrance and exit slits which were at ground potential, was made to have a triangular time variation at a frequency of 20 cps with an amplitude of several volts about a mean dc level. Any desired portion of an energy spectrum could thus be swept rapidly and repeatedly. The dc potential difference determined the absolute energy corresponding to the midpoint of the sweep, and the amplitude of the sweep voltage governed the range of energies focused; in normal operation this range was made to extend to an energy slightly higher than that of the primary electrons, so that the peak of elastically scattered electrons was fully traversed. A similar sweep voltage, of suitable (fixed) amplitude, was applied to the analog-to-digital converter circuitry of a multi-channel pulse-height analyzer.⁷ Pulses from the electron-multiplier detector after suitable amplification were also fed to the pulse-height analyzer, which stored a count coinciding with the detection of an electron in a channel appropriate to the energy of that electron as determined by the instantaneous value of the sweep voltage. A spectrum was thus built up, count by count, in the memory of the analyzer; voltage settings were generally such that the elastic peak appeared near channel number 20, with the energy-loss peaks occurring at higher channel numbers.

The sweep frequency was sufficiently high to ensure that essentially no change in the surface condition of the target would occur in the course of at least several sweeps of the spectrum. In practice, a spectrum was recorded in the first 200 channels of the analyzer for a

* Work supported by the U. S. Army Research Office and the University of Western Australia.

¹ J. L. Robins and P. E. Best, *Proc. Phys. Soc. (London)* **79**, 110 (1962).

² R. H. Ritchie, *Phys. Rev.* **106**, 874 (1957).

³ E. A. Stern and R. A. Ferrell, *Phys. Rev.* **120**, 130 (1960).

⁴ P. Nozières and D. Pines, *Phys. Rev.* **109**, 1062 (1958).

⁵ C. J. Powell and J. B. Swan, *Phys. Rev.* **115**, 869 (1959).

⁶ Model N 4035, Hamner Electronics Company Inc., Princeton, New Jersey.

⁷ Model 34-12, Radiation Instrument Development Laboratory, Chicago, Illinois.

period of one minute; storage was then switched to the second 200 channels, starting on each occasion with zero counts in this section of the memory. If this second spectrum agreed with the original in relative peak height and in the channel number of the peak of elastically scattered electrons, as determined by some ten seconds' observation of the live display, storage was switched back to the first 200 channels, and counts were added to those already in the memory there for a further period of one minute. In this way, intermittent checks on spectrum shape and elastic peak positions were maintained, and a run could be terminated at any time without loss or degradation of the spectrum already stored. Since the accuracy with which a peak position may be determined depends on the number of counts stored in each channel under that peak, a run which remained satisfactory was continued until sufficient counts in the peaks of interest had been accumulated.

In the mode of operation of the multichannel analyzer described above, the spectrum shape is distorted by dead-time effects at high count-rates; for this reason the count-rate was held well below the possible maximum, and runs of up to one hour were required. This in itself did not present any particular difficulty, but in future work it is intended to use the analyzer as a multiscaler, for in this mode the dead time is considerably less and runs of a few minutes will suffice to give results comparable with those to be presented below.

Following completion of each run, a sweep calibration was carried out. A spectrum, similar to that of the main spectrum, was recorded in the second 200 channels for a time sufficient to give good statistics for the elastic peak. The electron-gun accelerating voltage, corresponding to a primary electron energy of E_p eV, was then lowered by, say, 5 V (as accurately measured with a potentiometer, using a 1000:1 or 2000:1 voltage dividing network) and another spectrum in which the elastic peak appeared now at a higher channel number was added. This procedure was continued until the elastic peak lay in the region of channel number 180.

Data stored thus in all 400 channels were processed by a computer.⁸ The program, details of which will be published,⁹ used a method of repetitive curve fitting to locate peak positions and at the same time eliminated apparent peak-shift effects which result from the presence of a sloping background. The differences in channel number between the positions of the several elastic peaks in the calibration spectrum stored in the second 200 channels were used in measurement of the associated energy-loss spectrum stored in the first 200 channels. These elastic peaks could be located to within ± 0.05 channel, and the differences were found to lie within ± 0.4 channel of their mean. For the usual sweep amplitude the differences were about 50 channels for each 5-V primary-energy decrement, corresponding to

0.1 eV/channel. The incremental linearity of the sweep was thus found to be good to at least 1 part in 100, and the maximum error in energy arising from this source was less than 0.05 eV. Any error introduced by the primary-energy decrement, 5.000 ± 0.002 eV, was small by comparison. To preserve this accuracy when computing energy losses corresponding to channel differences of up to 200, a calibration value in eV/channel calculated to at least four significant figures was required; this value was obtained by a least-squares fit of a linear calibration to the calibration points. Loss peaks could not be located to better than ± 0.1 channel in general, the uncertainty increasing to ± 0.3 channel as the peak height above background decreased. Each individual energy-loss measurement may thus have a maximum error arising from these sources of approximately 0.1 eV. To avoid the introduction of rounding-off errors during computation, the computer was programmed to calculate each calibration to seven figures, and to give as a final output the energy difference in eV between the elastic peak and all other detectable peaks in a spectrum calculated to three decimal places.

RESULTS AND DISCUSSION

Spectra obtained using targets of sodium and potassium are shown in Figs. 1 and 2, respectively. The points are a plot on a logarithmic scale of the counts stored in each channel of the multichannel analyzer, for the primary-electron energies indicated. For each curve, the channel corresponding to the peak of elastically-scattered electrons has been located at the zero of the energy-loss scale, and the channel numbers have been multiplied by the appropriate calibration factor.

In the spectra of sodium taken at low primary energy the single surface loss (1S) and the single volume loss (1V) were well resolved. The sum peaks corresponding to 2S, 1S+1V, and 2V were also resolved. It is worth noting, though the matter is not pursued further in this investigation, that the ratio of the intensity of the double surface-loss peak, 2S, to that of the single

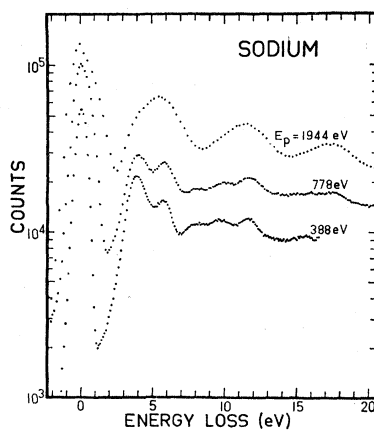


FIG. 1. Energy-loss spectra of sodium, for the primary energies indicated.

⁸ Model 1620, IBM (Australia).

⁹ B. M. Hartley and J. B. Swan (to be published).

TABLE I. Sodium energy-loss values, being the energy differences in eV between the elastic and other peaks in the spectra of sodium for the various primary energies E_p eV, computed to 3 decimal places; values in parentheses are those for peaks of low intensity. The assignments of the losses appear as column headings; for the primary energies of 1944 and 1962 eV the presence of unresolved surface components lowers the apparent volume-loss value.

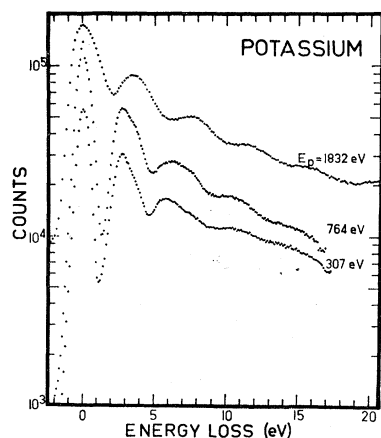
E_p	1S	1V	2S	S+V	2V	S+2V	3V	4V	5V	6V	7V
388	3.808	5.843	7.941	9.612	11.670
769	3.867	5.887	(7.9)	9.587	11.640	15.363	17.442
773	3.647	5.970	...	9.621	11.817	15.540	17.760
773	3.819	5.838	(7.8)	9.590	11.615	15.507	17.418
778	3.825	5.895	8.002	9.703	11.724	15.507	17.568
1944	...	5.344	11.408	...	17.327	23.238	29.172	34.897	(41.4)
1962	...	5.305	11.523	...	17.389	23.331

surface-loss peak, 1S, is apparently less than the ratio of 2V to 1V intensities. At higher primary energies, where the decreased relative intensity of the surface loss coupled with the relatively poorer instrumental resolution made separation of surface and volume

calculated to be $3.8_2 \pm 0.10$ eV, and that of the volume loss 5.85 ± 0.05 eV.

In none of the potassium spectra was the surface loss resolved. However, a regular change in the energy loss of the first loss peak was observed with changing primary energy, as is apparent from the values listed in Table II. From the appearance of this peak at low and intermediate primary energies in Fig. 2 it is evident that it consists of unresolved surface- and volume-loss peaks, the former being more intense at lower primary energy. The computed loss value of this peak increased from 2.73 eV at an electron-gun voltage of 307 V to 4.05 eV at 2514 V, and this is interpreted as resulting from changes in relative intensity of the surface and volume losses. A similar trend is apparent in the case of the second loss peak, which consists of the unresolved 2S, 1S+1V, and 2V peaks; at intermediate and high primary energies the intensity of the 2S loss would be expected to be relatively small if in potassium the rapid decrease in intensity of multiple surface losses is similar to that observed in sodium, and some support for this expectation is given by the observed breadth of this second peak. Under these conditions, subsequent peaks would also have their main intensity contribution from losses of the type $1S+(n-1)V$ and nV ; differences in loss value would then approximate the value of a single volume loss. The possibility that higher order losses may be nonintegral multiples of the first loss

FIG. 2. Energy-loss spectra of potassium, for the primary energies indicated.



components impossible, the observed loss peak was a combination of these, having a loss value biased towards the volume-loss value on account of the higher relative intensity of that component. Analysis of the data yielded the results for sodium listed in Table I. From these, the value of the surface loss in sodium is

TABLE II. Potassium energy-loss values. Figures in parentheses refer to diffuse peaks of low intensity having broad maxima within the ranges indicated. See text for discussion of column headings and of the trends in energy loss apparent in each column.

E_p (eV)	1S, 1V	2S, S+V, 2V	3S?	2S+V, S+2V, 3V	2S+2V S+3V, 4V	5V?
307	2.733	5.873	(7.7)	10.872	(13.5-16.5)	...
764	2.809	6.537	...	10.716	(13.7-16.1)	...
768	2.809	6.380	...	(9.5-11.5)	(13.5)	...
774	2.839	6.588	...	11.077	(13.5-15.4)	(18.6-20.6)
800	3.055	7.550	...	(10.5-11.5)	13.525	...
1156 ^a	3.253	7.639	...	(11.0-12.5)	(15.5-16.5)	...
1594	3.456	7.421	...	11.423	(14.3-17.6)	...
1832	3.693	7.822	...	11.858	16.068	(19.9-21.6)
2027	3.988	8.297	...	12.874	(15.7)	...
2087	3.741	7.717	...	11.717	15.494	...
2514	4.049	8.195	...	12.369	16.511	(20.770)

^a At this energy alone, and then only in some computations, was the first loss resolved into two peaks at approximately 2.85 and 4.30 eV.

cannot be excluded, and the possibility of a variation in loss energy with primary energy also exists; however, a combination of these possibilities, including also a variable nonintegral factor, would be required to describe the observations. On the other hand, this requirement is fulfilled by the simpler assumption of fixed values for a surface and a volume loss, together with sums and integral multiples of these. The value of the volume loss obtained from energy differences between loss peaks in spectra for primary energies above 2000 eV has a mean of 4.10 eV. If it is assumed that the intensity of losses of the type $1S + (n-1)V$ is relatively small at these primary energies, because of the relatively low probability of a $1S$ loss, a volume-loss value of 4.05 eV may be calculated from a weighted mean of $(nV)/n$ for $n > 1$ and $E_p > 2000$ eV. The value 4.05 ± 0.15 eV is therefore assigned to the volume loss in potassium.

The value of the surface loss in potassium is obtained from the measured energy difference between the elastic peak and the first loss peak at low primary energy, where it may be expected that the volume loss intensity will be relatively small. For $E_p < 800$ eV, the mean of such differences is 2.80 eV. Some further weight should also be attached to the value of 2.73 eV obtained at the lowest primary energy of 307 eV. The surface loss in potassium is thus allotted the value of $2.75_{-0.05}^{+0.10}$ eV.

Examination of Tables I and II shows that all observed peaks may reasonably be interpreted on the basis of the foregoing discussion and energy assignments. The agreement of the volume energy losses with the theoretical values and the optical measurements quoted by Nozières and Pines⁴ is satisfactory.

Turning now to the measurements by Robins and Best,¹ it would appear that the position of the first volume-loss peak in their spectra of both sodium and potassium was incorrectly located, in that insufficient allowance was made for the shift of the first volume-loss peak towards the elastic peak, arising from the presence of the surface loss peak. This is understandable when one considers that in sodium even the first surface- and volume-loss peaks were practically unresolved, partly because the measurements were made at primary energies now termed "intermediate" for which both

loss processes are roughly equally probable. A similar shift occurs for the successive volume-loss peaks, though relative to the energy loss of the peak this shift becomes progressively less significant. Differences between successive peaks would thus give approximately correct values for the energy of the volume plasmon excitation, and their values so obtained for sodium and potassium fall within the limits of the present work. It should be observed that, while their mean difference for the sodium volume losses was 5.87 eV, values of $(mV)/m$ obtained from their table of results increase steadily from 5.37 eV at $m=1$ to 5.78 eV at $m=6$; a corresponding observation may be made for their potassium results. For the case of the surface loss, it would appear that the first loss peak in sodium also has been incorrectly located, with too great a difference between it and the elastic peak. The difference between $1S+1V$ and $1V$, and also $1S+2V$ and $2V$, would likewise give too high a value for the energy of the surface loss.

CONCLUSION

Measurements of the characteristic electron energy-loss spectra of the alkali metals sodium and potassium have been carried out, and the results obtained are consistent with the assignment of intrinsic surface and volume energy losses of 3.82 ± 0.10 eV and 5.85 ± 0.05 eV in sodium, and $2.75_{-0.05}^{+0.10}$ eV and 4.05 ± 0.15 eV in potassium. Energy anomalies in the spectra of sodium were looked for but not found, and the spectra of potassium could be interpreted conventionally. Previously reported anomalies in the loss spectra of these metals¹ are thus here explained as arising from an underestimation of the peak shift due to the presence of unresolved components. The spectra at energy losses greater than those reported herein were observed to be in qualitative agreement with this previous work.

ACKNOWLEDGMENTS

The assistance provided by B. M. Hartley in preparing the computer program, and by D. H. Trout and others in maintenance of the apparatus, is gratefully acknowledged.