

changed by an amount

$$\delta b_{4s} = \frac{(H_{1,bb} - H_{1,aa})H_{1,ab}}{(E_{4s} - E_{3d})^2} = 7.5 \times 10^{-4}. \quad (26)$$

Upon including  $\delta b_{4s}$  and a term ( $\propto b_{4s}^2$ ) due to the normalization of the perturbed wave function, one obtains  $Q_{\text{ind}} = 0.303a_H^2$ , so that the correction to (24) is less than 3%. This conclusion depends, of course, on the value of  $E_{4s} - E_{3d}$ . If this energy difference were substantially less than 0.3 ry, the actual  $Q_{\text{ind}}$  would be appreciably smaller than the first-order result and would have to be obtained from an exact calculation of the 4s admixture.

As has been discussed in I, the induced quadrupole

moment contributes to the spectral term defects of the alkalis, for which it gives of the order of 10 to 30% of the amount contributed by the induced dipole moment.<sup>6</sup> The perturbed wave functions obtained in the present work may also be of interest in the construction of appropriate wave functions for polar molecules.<sup>16</sup>

#### ACKNOWLEDGMENTS

I wish to thank Dr. T. P. Das and Dr. E. G. Wikner for very helpful communications and for informing me of their results before publication. I am also very much indebted to Professor R. H. Dalitz for helpful discussions.

<sup>16</sup> L. C. Allen, *Bull. Am. Phys. Soc. Ser. II*, **2**, 43 (1957).

## Inelastic Scattering of 20-kev Electrons in Metal Vapors\*

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The low-energy losses of 20-kev electrons passing through the vapors of Zn, Cd, Hg, Na, K, Mg, Ca, Sb, Pb, and KCl, have been measured by using an electrostatic analyzer previously used for measuring electron energy losses in thin metal films. The atomic transitions corresponding to the measured energy losses are in many cases fairly easily established. However, there remain some which are questionable due to the fact that there is more than one feasible transition with energy differences of the order of the given energy loss. It is established that the principal interaction results in the excitation from the ground state of the neutral atom to the first excited level—the resonance excitation. It is also found that dipole excitations predominate

### INTRODUCTION

FROM the time that Franck and Hertz<sup>1</sup> first demonstrated in 1914 the existence of quantized inelastic collisions between electrons and gas atoms, many experiments were performed to measure such quanta of energy loss. This work was summarized up to 1925 by Compton and Mohler.<sup>2</sup> Brode,<sup>3</sup> in 1933, reviewed the study of the collisions of electrons with atoms, and more recently Massey and Burhop<sup>4</sup> have brought this information up to date. The energy losses have been called resonance losses and critical potentials. Most of the measurements were made for the permanent gases although a few were made for the metal vapors. All of these measurements were made at very low primary-electron energies, generally not extending beyond the value of the first ionization potential of the atom.

The measurements to be described were performed with primary electrons of 20-kev energy, principally because we were interested in obtaining the energy losses in metal vapors under the same conditions as our measurements previously reported<sup>5</sup> for the energy losses of 20–30 kev electrons in thin metal films.<sup>6</sup> With high-energy electrons one is not limited, in principle, to exciting only dipole and higher multipole transitions as is the case with electromagnetic radiation; it should be possible to excite monopole transitions as well.<sup>7</sup> However, the Born approximation predicts that dipole excitations of the atomic electrons should predominate. Fano<sup>8</sup> has described the relative probabilities of excitation and ionization when a high-energy electron (1–100 kev) interacts with hydrogen atoms. In Fig.

\* This work was supported in part by the U. S. Atomic Energy Commission.

<sup>1</sup> J. Franck and G. Hertz, *Verhandl. deut. physik. Ges.* **16**, 457 (1914).

<sup>2</sup> K. T. Compton and F. L. Mohler, *National Research Council (U.S.) Bull.* **48**, Vol. 9 (1924–1925).

<sup>3</sup> R. B. Brode, *Revs. Modern Phys.* **5**, 257 (1933).

<sup>4</sup> H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1952).

<sup>5</sup> Marton, Leder, and Mendlowitz in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 183.

<sup>6</sup> E. J. Sternglass, *Nature* **178**, 1387 (1956), has stated that measurement of the energy losses of electrons in metal vapors may provide a test for distinguishing between individual atomic and collective losses of electrons in thin solid films.

<sup>7</sup> In what follows, all transitions other than dipole will be referred to as optically forbidden or forbidden transitions.

<sup>8</sup> U. Fano in *Radiation Biology*, edited by A. Hollaender (McGraw-Hill Book Company, Inc., New York, 1954), Vol. 1, p. 56.

1-38(a) of his article<sup>8</sup> it is shown that the probability of excitation of the first excited level should be appreciably greater than for any other inelastic interaction. It is also shown that the total probability for all other excitations is still slightly greater than for ionization. It was our purpose to determine whether the most prominent excitation would be to the first excited level.

We have attempted to determine exactly which other transitions in the metal vapor result in the energy losses found by us. It will be seen that this is not always possible to do since there are many cases where more than one type of transition can be a feasible cause of the energy loss.

#### APPARATUS AND EXPERIMENTAL METHODS

The apparatus used for these measurements was essentially the same as that used by us for the measurements of the characteristic energy losses of electrons described in some detail previously.<sup>5</sup> The object chamber of the earlier apparatus was replaced for these measurements by an oven chamber for producing the metal vapor. A diagram of the arrangement is shown on Fig. 1. A 20-kev electron beam generated by the electron gun passed through two apertures in the oven wall, encountering the metal vapor in the process. The electrons then entered the analyzer, which was of the Mollenstedt type,<sup>9</sup> through a 5-micron slit where they were separated into the component velocities. The analyzer had a resolution of approximately 1 ev at 20 kev. The energy-loss spectra were recorded on a photographic plate and then traced by means of an automatic recording microphotometer.

The oven assembly was fashioned somewhat after that described by Lew<sup>10</sup> and is shown on Fig. 2. The oven itself was made from a Monel rod  $\frac{1}{2}$  inch in diam-

eter and the inside removed to leave a 0.010-inch wall. At one end a  $\frac{1}{4}$ -inch shaft  $\frac{7}{8}$  inch long was left for making electrical connection to the oven. The other end was fitted with a plug having a  $\frac{1}{4}$ -inch shaft  $1\frac{3}{8}$  inches long. Perpendicular to the axis of the oven and at the center two 0.010-inch holes were drilled through the oven wall through which the electron beam could pass. The unit was clamped on the  $\frac{1}{4}$ -inch shafts between copper blocks soldered to copper tubing going back to the mounting plate. To allow for expansion of the oven, one clamp was left slightly loose and was connected by a strap to another clamp on the oven shaft making electrical connection. The copper tubing was used to carry electrical power to the oven, one pair of the tubes being insulated from the mounting plate, and to cool the copper mounting blocks as well as the tubing itself. The assembly at the mounting-plate end was such that the oven could be rotated as well as moved in and out

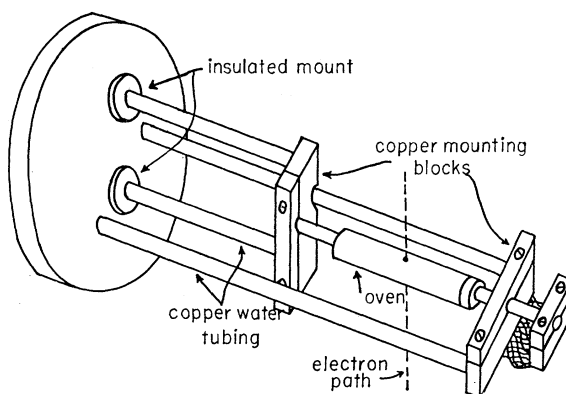


FIG. 2. Oven assembly showing the method of mounting and the current and cooling leads.

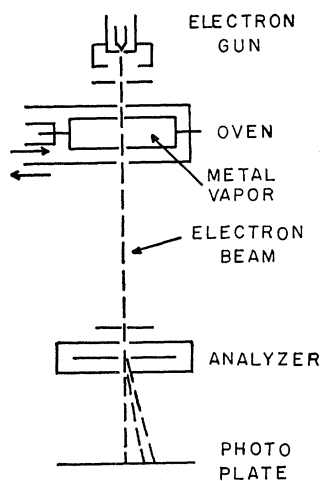


FIG. 1. Diagram of apparatus for measuring energy losses of electrons in metal vapors.

<sup>9</sup> G. Mollenstedt, *Optik* 5, 499 (1949).

<sup>10</sup> H. Lew, *Phys. Rev.* 91, 619 (1953).

in order to position the 0.010-inch apertures with respect to the electron beam.

A current of 200 amperes at 5 volts could bring the oven to a temperature of approximately 1000° C. This power was obtained from a half-wave rectifier with a maximum output of 200 amperes at 10 volts. The metal to be evaporated was placed in the oven in contact with the oven wall except in the case of the mercury measurements where a ceramic boat was used to hold the mercury. The hottest part of the oven was at the center where the 0.010-inch apertures were located so that no clogging of these apertures resulted. Condensation of the residual metal generally occurred at the ends of the oven when the oven was brought to room temperature.

Since we were only interested in obtaining energy-loss values and their relative intensities the pressure of the metal vapor was not accurately controlled or measured. A rough calculation indicated that to obtain approximately the same number of atoms in the half-inch path length as would be encountered in 100 angstroms of a solid film it was necessary to operate at a point on the

vapor-pressure curve where the temperature in degrees centigrade was numerically approximately one-eighth the vapor pressure in microns. The oven current was therefore brought to a point where the temperature was estimated from the color of the oven as being the one desired. Because of the magnetic field produced by the current passing through the oven and because of the expansion of the oven due to heating, it was found that the electron gun had to be adjusted under operating conditions to bring the electron beam through the two 0.010-inch apertures of the oven with maximum intensity. After this adjustment was made, several photographic exposures were made with different time exposures varying from 15 seconds to 2 minutes in order to obtain measurements of both the strongest and weakest energy-loss lines. The photographic plates were then traced with a microphotometer, and the energy-loss values determined from these traces. A photograph of the calcium energy-loss spectrum is shown on Fig. 3. The series of equally spaced lines to the right are the 6-volt calibration markers and the lines on the left represent the energy losses, with the uppermost line the zero loss line.

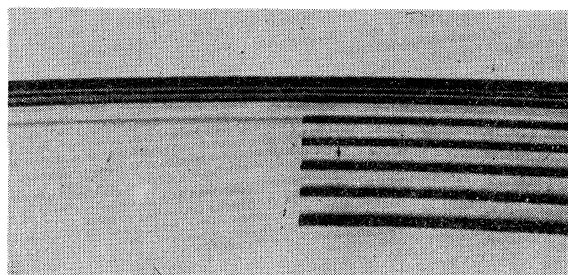


FIG. 3. Photograph of the calcium energy-loss spectrum. The series of equally spaced lines on the right are the 6-volt calibration markers, and the lines on the left represent the energy losses with the uppermost line the zero loss line.

Before each run on a metal sample the empty oven was heated in vacuum to approximately 1000° C for several minutes to assure that the oven was clean. It was also found necessary to operate at a vacuum of  $1 \times 10^{-5}$  mm Hg or better in order not to obtain energy losses in the residual air of the vacuum. At a pressure of greater than  $1 \times 10^{-5}$  mm Hg, an energy loss of 12.9 ev was obtained which was attributed to the residual nitrogen in the system.<sup>11</sup> Despite our precautions, it is believed that some of the energy losses found at approximately this value in the metal vapors may be due to this cause.

Several sources of error entered into the measurements. The calibration voltages were obtained from a bank of 6-volt batteries. Their values were measured with a Millivac model MV-17B vacuum-tube voltmeter which was calibrated with a Leeds and Northrup potentiometer. The smallest division on the scale used was 0.2 volt so that we can estimate an error in reading of 0.02 volt. This would give 0.33% error in a 6-volt reading. Another source of error was in estimating the centers of the loss lines and calibration lines. An estimate of this error would be on the order of 0.2 mm. Since the calibration was approximately 0.25 volt/mm (depending on the setting of the analyzer slit) this would give an error of approximately 0.05 volt or 0.83% error in a 6-volt loss. Finally there was the error in reading the scale with which the distances between peaks was measured. This error was also estimated as 0.2 mm so that from this source there was an additional error of 0.83%. The total error from all these sources could, therefore, be on the order of 2%. One other source of error was not corrected for except as noted in

<sup>11</sup> E. Rudberg, Proc. Roy. Soc. (London) **A129**, 628 (1930).

the discussion of the results. This occurred when two loss lines lay close to each other. If both losses were of nearly equal intensity, then the trace would tend to show them drawn together so that the low-lying one would be somewhat higher and the high-lying one somewhat lower. If one loss was weaker than the other, the weaker one would appear at a higher value in the tracing if it was on a rising slope of the strong loss and lower if it was on a decreasing slope of the strong loss.

All of the energy-loss distributions shown are composite figures. They are made up from three to six different microphotometer traces of photographs made at several different time exposures. The vertical scales of intensity are not significant since they represent the somewhat logarithmic microphotometer response to the photographic plates.

## RESULTS

### 1. Zinc, Cadmium, and Mercury

The outer structures of the atoms of these three materials are similar since they have a filled  $3d$  level and two  $s$  electrons. Because of this similarity in structure, we might expect the energy losses in their vapors to be similar. For this reason we discuss them together, and make some attempt to use the data from all three metal vapors to clarify the explanations of the individual losses. The energy-loss spectra are shown in Figs. 4, 5, and 6. The first energy loss in Hg is at 4.9 ev which corresponds<sup>12</sup> to the intercombination transition  $6^1S_0 \rightarrow 6^3P_1^0$ . This transition has a low probability as seen from Fig. 6. In the cases of Zn and Cd the corresponding transition was not observed. The next energy losses are the most probable for all three vapors. In the case of Hg it is quite evident that the 6.6-ev loss is due to the transition from the ground state of the neutral atom to the  $6^1P_1^0$  level. No energy loss corresponding to the transition from the ground state of the ionized atom to the  $6^2P_{3/2}^0$  level (7.5 ev) was found. In the cases of Zn and Cd this transition in the ionized atom is much

<sup>12</sup> All of the energy level values used in the following discussion are taken from *Atomic Energy Levels*, National Bureau of Standards Circular No. 467, edited by C. E. Moore (U. S. Government Printing Office, Washington, D.C., 1948).

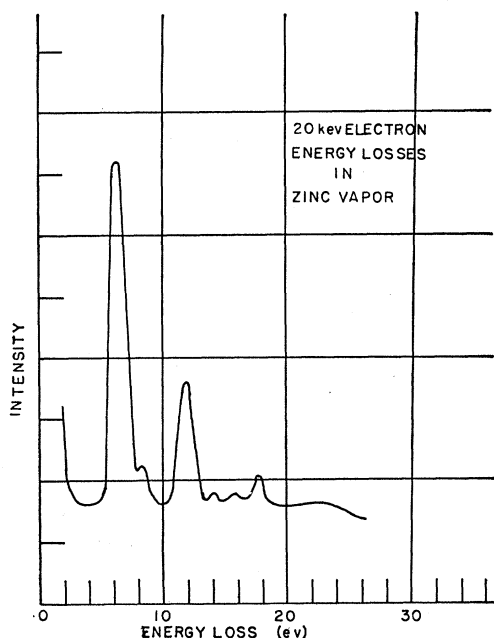


FIG. 4. Energy-loss distribution of 20-keV electrons in zinc vapor. The ordinate marked "intensity" represents the intensity in terms of the logarithmic response of the microphotometer to the photographic plate.

closer in value to the first transition in the neutral atom, so we must take these into account as being possible explanations of the 5.9-eV losses in Zn and Cd. However, on the basis of the Hg data, the first transition in the ionized atom must have a very low probability so that we assign the 5.9-eV losses in Zn and Cd to the

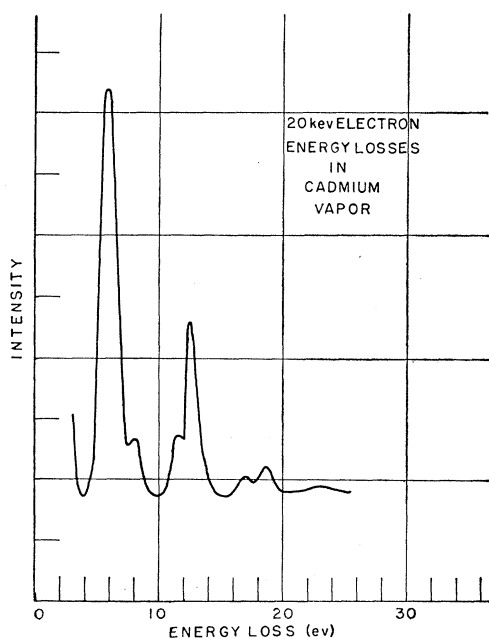


FIG. 5. Energy-loss distribution of 20-keV electrons in cadmium vapor.

neutral-atom transitions  $4^1S_0 \rightarrow 4^1P_1^0$  and  $5^1S_0 \rightarrow 5^1P_1^0$ . The next loss in Hg at 9.8 eV has been explained in several ways in the past. Foard<sup>13</sup> attributes this loss to two excitations of the 4.9-eV type while Vetterlein<sup>14</sup> states that this loss is due to the average of the excitations to the  $8^1P_1^0$  (9.7 eV) and  $9^1P_1^0$  (9.9 eV) levels. The explanation of Foard does not appear to be suitable since the 9.8-eV loss has a higher probability than the 4.9-eV loss. This is also borne out by the Zn and Cd data since the 7.8-eV loss in Zn and the 8.0-eV loss in Cd, which are similar to the 9.8-eV loss in Hg, appear while the intercombination losses corresponding to the 4.9-eV loss of Hg do not appear. The Vetterlein explanation is perhaps closer to the correct answer (his  $8^1P_1^0$

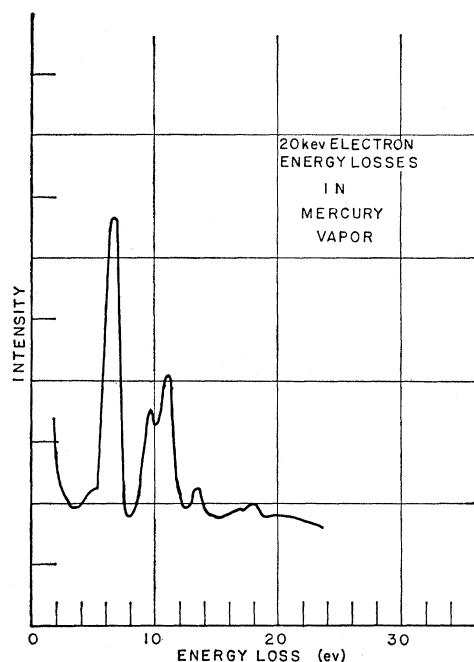


FIG. 6. Energy-loss distribution of 20-keV electrons in mercury vapor. The ordinate is the same as in Fig. 5.

value which he calls  $4^1P_1^0$  is incorrect) although it is our belief that this loss can be explained by the single transition  $6^1S_0 \rightarrow 8^1P_1^0 = 9.5$  eV. The equivalent transition can also explain the 8.0-eV loss found in Cd. However, for Zn the 7.8-eV loss is best explained by the transition  $4^1S_0 \rightarrow 5^1P_1^0$ . Why this discrepancy occurs is not at all clear at this time.

The second most probable energy losses found were those at 11.8 eV in Zn, 12.9 eV in Cd, and 11.0 eV in Hg. In each case the transition  $n^1S_0 \rightarrow n'^3P_1^0$  ( $n=4, 5,$  and  $6$  for Zn, Cd, and Hg, respectively) is very close to the measured values. This is an inner shell excitation (from the  $d$  shell instead of the  $s$  shell). There are other possible transitions which would give values of the order

<sup>13</sup> C. W. Foard, Phys. Rev. **35**, 1187 (1930).

<sup>14</sup> P. Vetterlein, Ann. Physik **35**, 187 (1939).

TABLE I. Energy losses of 20-kev electrons in zinc vapor. The first two columns give the transitions from the ground state of the neutral atom and ionized atom to the designated excited states. The third column gives the corresponding excited-level energies, and the fourth column the measured energy losses.

Neutral atom 4 <sup>1</sup> S <sub>0</sub> to	Ionized atom 4 <sup>2</sup> S <sub>1/2</sub> to	Excited level (ev)	Energy loss (ev)
4 <sup>1</sup> P <sub>1</sub> <sup>0</sup>	4 <sup>2</sup> P <sub>3/2</sub> <sup>0</sup>	5.8	5.9
5 <sup>1</sup> P <sub>1</sub> <sup>0</sup>		6.1	
2 × (4 <sup>1</sup> P <sub>1</sub> <sup>0</sup> )		7.8	7.8
4' <sup>3</sup> P <sub>1</sub> <sup>0</sup>		11.6	11.8
4 <sup>1</sup> P <sub>1</sub> <sup>0</sup> + 5 <sup>1</sup> P <sub>1</sub> <sup>0</sup>		11.7	
2 × (5 <sup>1</sup> P <sub>1</sub> <sup>0</sup> )		13.6	13.7
3 × (4 <sup>1</sup> P <sub>1</sub> <sup>0</sup> )		15.6	15.4
4 <sup>1</sup> P <sub>1</sub> <sup>0</sup> + 4' <sup>3</sup> P <sub>1</sub> <sup>0</sup>		17.4	17.3
4 × (4 <sup>1</sup> P <sub>1</sub> <sup>0</sup> )		17.5	22.7
		23.2	

of magnitude of the measured ones. The only other one common to all three metals is the transition  $n^1S_0 \rightarrow (n+1)'^1P_0$  (which also is an inner-shell excitation), but in each case it appears to be too much different from the measured values to be a likely explanation for the energy loss. For Zn it is 0.65 ev too low, for Cd 0.8 ev too low, and for Hg 0.35 ev too high. In the case of Zn there is undoubtedly a contribution from two of the first dipole transitions in the neutral atom since this should occur at 11.6 ev. It is also probable that the next losses in Cd and Hg at 11.2 ev and 13.2 ev, respectively, are also due to two such transitions. The 13.7-ev loss in Zn and the 16.4-ev loss in Hg appear to be due to the first dipole transition plus the second dipole transition of the neutral atom. These sums give 13.6 ev and 16.2 ev compared to the measured losses of 13.7 ev and 16.2 ev. We did not find a similar energy loss (which should have occurred at 13.5 ev) in Cd vapor. This was probably due to the fact that the strong 12.9-ev loss lies so close to the value of this loss that we could not resolve it. In the case of Hg there are several forbidden transitions in the ionized atom which may contribute to the 16.4-ev loss. For Zn similar forbidden transitions may account for the 15.4-ev loss, although two transitions of the type  $4^1S_0 \rightarrow 5^1P_1^0$  also are equal to 15.6 ev. Here again it appears that two transitions contribute to the energy loss. In the case of Cd no energy loss corresponding to the above forbidden transitions in the ion was found.

TABLE II. Energy losses of 20-kev electrons in cadmium vapor. The column headings are the same as for Table I.

Neutral atom 5 <sup>1</sup> S <sub>0</sub> to	Ionized atom 5 <sup>2</sup> S <sub>1/2</sub> to	Excited level (ev)	Energy loss (ev)
5 <sup>1</sup> P <sub>1</sub> <sup>0</sup>	5 <sup>2</sup> P <sub>3/2</sub> <sup>0</sup>	5.4	5.9
7 <sup>1</sup> P <sub>1</sub> <sup>0</sup>		5.8	
2 × (5 <sup>1</sup> P <sub>1</sub> <sup>0</sup> )		8.1	8.0
5' <sup>3</sup> P <sub>1</sub> <sup>0</sup>		10.8	11.2
2 × (7 <sup>1</sup> P <sub>1</sub> <sup>0</sup> )		12.8	12.9
3 × (5 <sup>1</sup> P <sub>1</sub> <sup>0</sup> )		16.2	16.6
5 <sup>1</sup> P <sub>1</sub> <sup>0</sup> + 5' <sup>3</sup> P <sub>1</sub> <sup>0</sup>		16.2	
4 × (5 <sup>1</sup> P <sub>1</sub> <sup>0</sup> )		18.2	18.3
		21.6	22.8

TABLE III. Energy losses of 20-kev electrons in mercury vapor. The column headings are the same as for Table I.

Neutral atom 6 <sup>1</sup> S <sub>0</sub> to	Ionized atom 6 <sup>2</sup> S <sub>1/2</sub> to	Excited level (ev)	Energy loss (ev)
6 <sup>3</sup> P <sub>1</sub> <sup>0</sup>		4.9	4.8
6 <sup>1</sup> P <sub>1</sub> <sup>0</sup>		6.7	6.6
8 <sup>1</sup> P <sub>1</sub> <sup>0</sup>		9.5	9.8
6' <sup>3</sup> P <sub>1</sub> <sup>0</sup>		11.0	11.0
2 × (6 <sup>1</sup> P <sub>1</sub> <sup>0</sup> )		13.4	13.2
6 <sup>1</sup> P <sub>1</sub> <sup>0</sup> + 8 <sup>1</sup> P <sub>1</sub> <sup>0</sup>		16.2	16.4
6 <sup>1</sup> P <sub>1</sub> <sup>0</sup> + 6' <sup>3</sup> P <sub>1</sub> <sup>0</sup>		17.7	17.7
3 × (6 <sup>1</sup> P <sub>1</sub> <sup>0</sup> )		20.1	20.2

In order to account for the energy loss of 16.6 ev in Cd we assume two transitions of the type  $5^1S_0 \rightarrow 7^1P_1^0$  (16.2 ev). Another way of explaining this loss would be to postulate three of the first dipole transitions in the neutral atom (also equal to 16.2 ev). Again it is possible that the energy loss observed is a superposition of both types of events. This is somewhat borne out by the next group of energy losses in all three metal vapors which seem to be clearly due to the sum of the first neutral-atom dipole transition plus the transition  $n^1S_0 \rightarrow n'^3P_1^0$  ( $n=4, 5, \text{ and } 6$ ). In the case of Zn we superimpose three of the first neutral-atom dipole transitions (equal to 17.4 ev). The same three transitions account for the 20.1-ev loss in Hg. The last energy losses found in Zn and Cd are probably accounted for by four of the above transitions. These were quite weak in the photographic plate and so their accuracy is considerably less than for the other losses. The results are given in Tables I, II, and III.

2. Sodium and Potassium

The low-lying losses in Na and K vapor can be assigned to transitions in the neutral atom. However, in both materials, particularly in K, there are a number of large losses which can only be explained by transitions in the ionized atom. Unfortunately, the data on the atomic energy levels<sup>12</sup> in the ionized atom are incomplete, and, therefore, the assignments are open to question. The first, and strongest, loss in each metal vapor is due to the transition  $n^2S_{1/2} \rightarrow n^2P_{3/2}^0$  ( $n=3 \text{ and } 4$ ). The second energy loss is not so easily determined since

TABLE IV. Energy losses of 20-kev electrons in sodium vapor. The column headings are the same as for Table I.

Neutral atom 3 <sup>2</sup> S <sub>1/2</sub> to	Ionized atom 2 <sup>1</sup> S <sub>0</sub> to	Excited level (ev)	Energy loss (ev)
3 <sup>2</sup> P <sub>3/2</sub> <sup>0</sup>		2.1	2.3
5 <sup>2</sup> P <sub>3/2</sub> <sup>0</sup>		4.3	
5 <sup>2</sup> S <sub>1/2</sub>		4.1	4.3
4 <sup>2</sup> D <sub>3/2</sub>		4.3	
2 × (3 <sup>2</sup> P <sub>3/2</sub> <sup>0</sup> )		4.2	6.3
3 × (3 <sup>2</sup> P <sub>3/2</sub> <sup>0</sup> )		6.3	
3 <sup>2</sup> P <sub>3/2</sub> <sup>0</sup> + 4.3		6.4	~31
	L <sup>1</sup>	~33	
3 <sup>2</sup> P <sub>3/2</sub> <sup>0</sup>	L <sup>1</sup>	~35	~34

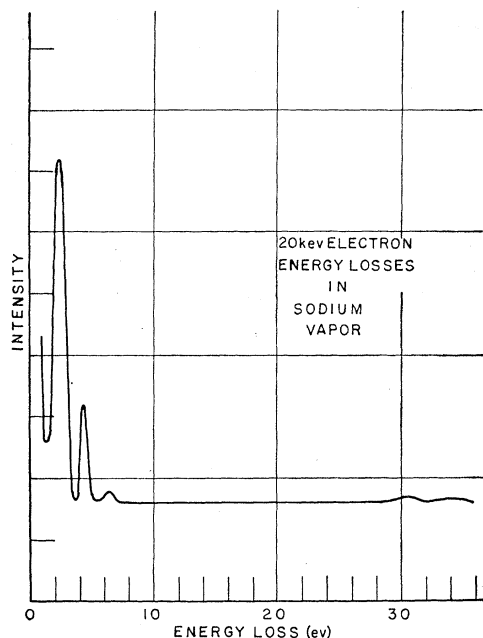


FIG. 7. Energy-loss distribution of 20-keV electrons in sodium vapor. The ordinate is the same as in Fig. 5.

there are several feasible transitions, both dipole and monopole, lying very close together. Since the first loss has such a high probability, it is most likely that what we have observed is the sum of two of the first transitions superimposed on the weaker transitions  $n^2S_{3/2} \rightarrow (n+2)^2P_{3/2}^0$ . Whether the forbidden transitions shown in Table IV contribute to this loss cannot be stated with certainty.

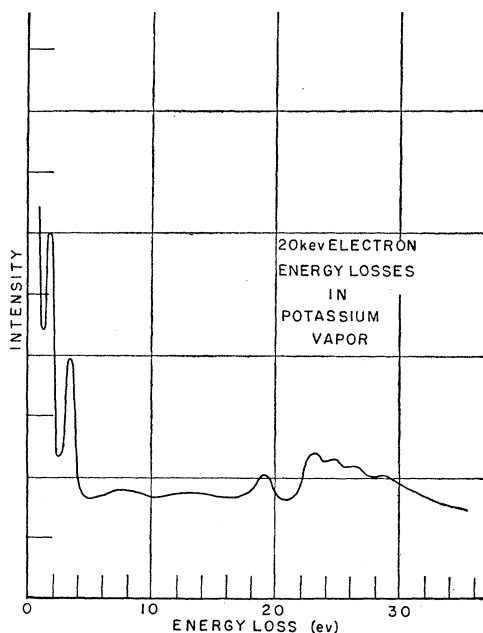


FIG. 8. Energy-loss distribution of 20-keV electrons in potassium vapor. The ordinate is the same as in Fig. 5.

All of the next energy losses are above the first ionization potential. The 6.3-eV loss in Na can probably be accounted for as being due either to three of the first transition, or, if the second loss is not due to two such transitions, as the sum of the first transition plus the second. In K the 7.8-eV loss is considerably greater than three of the first losses so that this loss does not correspond to the Na loss of 6.3 eV. The only possibility that we can find is that it may be due to one loss of the first kind (1.6 eV) plus two of the second (3.3 eV) giving a total loss of 8.2 eV. This assumes, as was done above for Na, that the second loss is not due to two of the first dipole excitations in the neutral atom. The 13.0-eV loss cannot be explained in terms of the earlier losses, and is also too low to be due to inner-shell excitation. It is possible that it is due to some double excitation process for which the level is not given in the tables, or it may be due to excitation in the residual gas of the vacuum as pointed out earlier.

Since the designations for the levels in the ionized atoms of Na and K are given in *Atomic Energy Levels*<sup>12</sup> in  $jl$  coupling notation, we shall, for convenience of discussion, designate the levels as  $L^1, L^2$ , etc. The outermost configuration of ionized Na is  $2p^6$ , and the first excitation (denoted by  $L^1$ ) will change this configuration to  $2p^5s$ . The energy value for this is given as  $\sim 33$  eV. Therefore, we will consider the measured loss of  $\sim 31$  eV as being due to this excitation. The energy loss of  $\sim 34$  eV is then considered as being due to the sum of two excitations, the first one in the neutral atom plus that due to  $L^1$  in the ionized atom.

In K we find several more ionized-atom losses than in Na. The first three levels in ionized K we will designate as  $L^1$  ( $3p^53d$  and  $3p^54s$ ),  $L^2$  ( $3p^54p$ ), and  $L^3$  ( $3p^54d$  and  $3p^55s$ ). The outermost configuration of singly ionized K is  $3p^6$ . The energy loss of 19.0 eV can be explained as being due to the average of two excitations. The first is an inner-level excitation in the neutral atom,  $1^2S_{3/2} \rightarrow 2'^2P_{3/2}^0 = 18.7$  eV, and the second is to  $L^1$  ( $\sim 20.5$  eV). The second loss in the high loss group at 22.8 eV

TABLE V. Energy losses of 20-keV electrons in potassium vapor. The column headings are the same as for Table I.

Neutral atom $4^2S_{3/2}$ to	Ionized atom $3^1S_0$ to	Excited level (eV)	Energy loss (eV)
$4^2P_{3/2}^0$		1.6	1.7
$6^2P_{3/2}^0$		3.6	3.3
$6^2S_{3/2}$		3.4	
$4^2D_{5/2}$		3.4	
$2 \times (4^2P_{3/2}^0)$		3.2	
$4^2P_{3/2}^0 + 2 \times (3.3)$		8.2	7.8
?		?	13.0
$4^1P_{3/2}^0$		18.7	19.0
	$L^1$	$\sim 20.5$	
$4^2P_{3/2}^0 +$	$L^1$	$\sim 22$	22.8
	$L^2$	$\sim 23$	
$4^2P_{3/2}^0 +$	$L^2$	$\sim 24.5$	24.6
	$L^3$	$\sim 26.5$	26.2
$4^2P_{3/2}^0 +$	$L^3$	$\sim 28$	28.5

is due to excitation to  $L^2$  ( $\sim 23$  ev) with, possibly, some influence from the sum of the first neutral-atom excitation and the excitation to  $L^1$  (total of  $\sim 22$  ev). The third loss of 24.6 ev is accounted for by the sum of the first neutral-atom excitation plus the excitation to  $L^2$ . The next loss of 26.2 ev is accounted for by the excitation to  $L^3$ , and the last loss of 28.5 ev is attributed to the first neutral-atom excitation plus the excitation to  $L^3$ . We have listed the energy-loss values and the possible levels for Na and K in Tables IV and V. The energy-loss spectra are shown in Figs. 7 and 8.

### 3. Magnesium and Calcium

Although Mg and Ca are in the same group of the periodic table, we should not expect their behavior to be entirely similar since the outer level structure is somewhat different. In Mg the outer levels are  $2p^6 3s^2$  and in Ca they are  $3p^6 4s^2$ , with the difference that in Ca there is a  $3d$  level between the  $3p$  and  $4s$  levels. The energy-loss spectra are given in Figs. 9 and 10. In the case of Ca it is fairly clear-cut that the first loss is due solely to the resonance transition  $4^1S_0 \rightarrow 4^1P_1^0$ , although one must consider the first dipole transition in the ion  $4^2S_{1/2} \rightarrow 4^2P_{3/2}^0$  as possibly contributing to the loss. For Mg these two transitions lie much closer together being  $3^1S_0 \rightarrow 3^1P_1^0 = 4.3$  ev and  $3^2S_{1/2} \rightarrow 3^2P_{3/2}^0 = 4.4$  ev. The 6.4-ev loss in Mg appears to be due either to the forbidden transition  $3^1S_0 \rightarrow 5^1S_0 = 6.5$  ev or  $3^1S_0 \rightarrow 4^1D_2 = 6.6$  ev while the 4.5-ev loss<sup>15</sup> in Ca appears to be due to the forbidden transition  $4^1S_0 \rightarrow 4^1D_2 = 4.6$  ev although the forbidden transition  $4^1S_0 \rightarrow 5^1S_0 = 4.1$  ev may also contribute. The Ca loss of 6.0 ev and the Mg loss of 8.7 ev are believed to be due to two of the first dipole transitions. There is also the possibility that two of the first dipole excitations in the ion may enter into these losses.

The final loss found in Mg is not easily explained, but may be due to some combination of the transitions indicated in Table VI. The 8.0-ev loss in Ca is a weak

TABLE VI. Energy losses of 20-kev electrons in magnesium vapor. The column headings are the same as for Table I.

Neutral atom $3^1S_0$ to	Ionized atom $3^2S_{1/2}$ to	Excited level (ev)	Energy loss (ev)
$3^1P_1^0$	$3^2P_{3/2}^0$	4.3	4.4
		4.4	
$5^1S_0$		6.5	6.4
$4^1D_2$		6.6	
$2 \times (3^1P_1^0)$	$2 \times (3^2P_{3/2}^0)$	8.6	8.7
		8.8	
$3 \times (3^1P_1^0)$	$3 \times (3^2P_{3/2}^0)$	12.9	13.4
		13.2	
$2 \times (5^1S_0)$		13.0	
$2 \times (4^1D_2)$		13.2	

<sup>15</sup> Although we give 4.5 ev as the value of this loss, its actual value is probably several tenths of a volt less since the loss line appears on the rising slope of the following strong loss line at 6.0 ev.

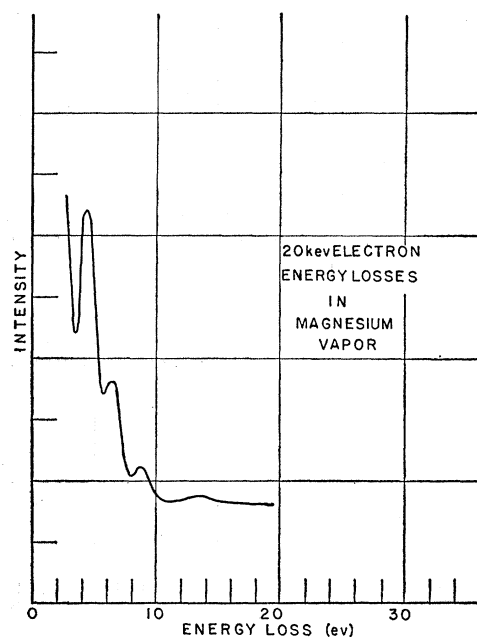


FIG. 9. Energy-loss distribution of 20-kev electrons in magnesium vapor. The ordinate is the same as in Fig. 5.

broad line showing some asymmetry. For this reason, we believe that it may be the result of the superposition of the three widely spread transitions shown in Table VII. It is also possible that this loss and the following one at 12.1 ev may be due to double excitation processes for which values have not been given in the levels tables. Two losses found in Ca at 30.9 and 33.0 ev are

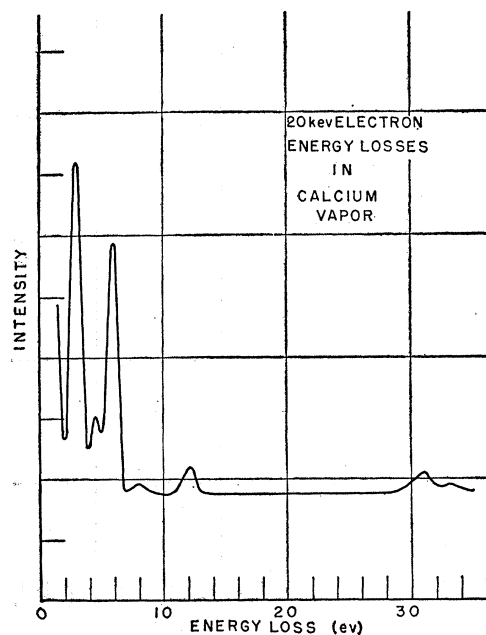


FIG. 10. Energy-loss distribution of 20-kev electrons in calcium vapor. The ordinate is the same as in Fig. 5.

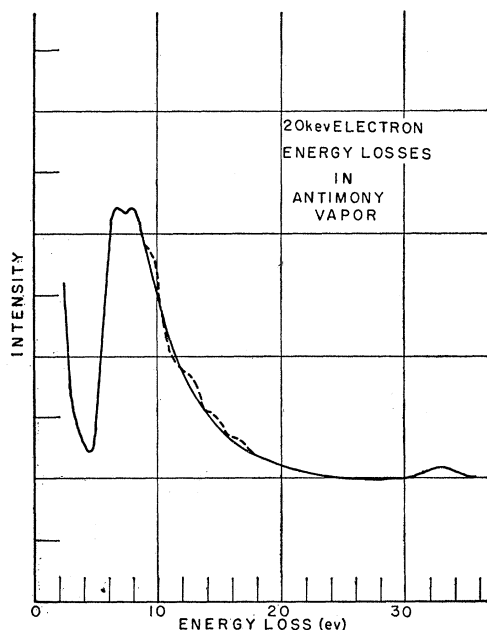


FIG. 11. Energy-loss distribution of 20-keV electrons in antimony vapor. The dashed lines show the positions of several loss peaks which were weak and could not be reproduced consistently. The ordinate is the same as in Fig. 5.

probably due to inner-shell excitation. For instance, there is given in the atomic levels tables an inner-shell transition for potassium where one of the  $3p$  electrons is excited to the  $4s$  level. This requires 19.7 ev. Since the  $4s$  level in neutral Ca is filled, a similar excitation would be from the  $3p$  level to the  $4p$  level so that the excited-

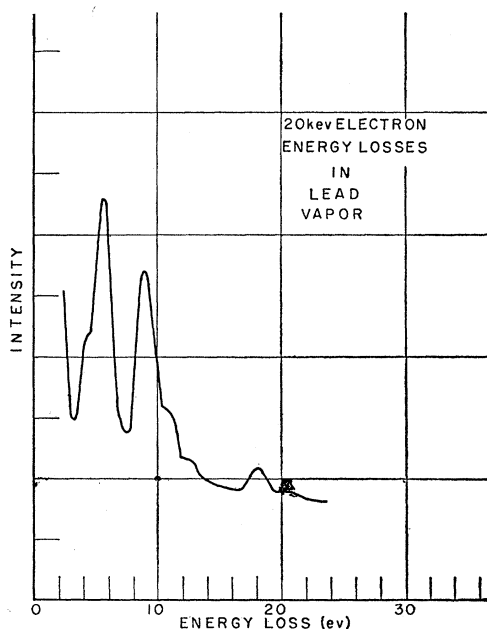


FIG. 12. Energy-loss distribution of 20-keV electrons in lead vapor. The ordinate is the same as in Fig. 5.

atom configuration would then be  $3p^5 4s^2 4p$ . Such a transition could reasonably require the 30.9 ev which we have found as a loss of the primary electron. The 33.0-ev loss could then be explained in the same way as an excitation of the  $3p$  electron to the  $4d$  level which would require on the order of two volts more than excitation to the  $4p$  level.

#### 4. Antimony

The energy-loss spectrum in antimony vapor is shown in Fig. 11. The two losses appearing at 6.7 and 7.9 ev are of the same intensity and lie close together. Under such conditions there is a tendency for the loss lines to "draw together" due to overlap of the tails of the individual distributions. If this were corrected for, the 6.7-ev loss would be several tenths of a volt less and the 7.9-ev loss several tenths of a volt higher. The first loss is due to the transitions  $5^4S_{3/2}^0 \rightarrow 2^4P_{3/2}$  in the

TABLE VII. Energy losses of 20-kev electrons in calcium vapor. The column headings are the same as for Table I. The last two lines represent the inner-shell excitations.

Neutral atom $4^1S_0$ to	Ionized atom $4^2S_{1/2}$ to	Excited level (ev)	Energy loss (ev)
$4^1P_1^0$		2.9	2.9
	$4^2P_{3/2}^0$	3.2	
$5^1S_0$		4.1	4.5
$4^1D_2$		4.6	
$2 \times (4^1P_1^0)$		5.8	6.0
	$2 \times (4^2P_{3/2}^0)$	6.4	
	$5^2S_{1/2}$	6.5	8.0
$3 \times (4^1P_1^0)$		8.7	
$2 \times (5^1S_0)$		8.2	8.0
$4^1P_1^0 + 5^1S_0$		7.0	
?		?	12.1
$3p^6 4s^2 \rightarrow 3p^5 4s^2 4p$			30.9
$3p^6 4s^2 \rightarrow 3p^5 4s^2 4d$			33.0

neutral atom. The second transition in the neutral atom requires 7.9 ev and the first transition in the ionized atom,  $5^3P_0 \rightarrow 5^3D_1^0$  requires 8.2 ev. It would appear that the second energy loss of 7.9 ev is due to the second neutral-atom transition except for the fact that the second loss is probably closer to the 8.2-ev value when corrected and that it is unlikely that the second transition in the neutral atom would have the same probability as the first. There is also the possibility that this loss is due to a combination of the neutral-atom and ionized-atom excitation. The loss of 33 ev is probably due to an inner-shell excitation. The x-ray levels for the  $N_4$  and  $N_5$  absorptions are given<sup>16</sup> as 32 and 33 ev, so that the loss we have measured is probably due to one of these. This would be an excitation of one of the  $4d$  electrons.

Several other weak loss lines were observed, but could not be repeated with consistency. The spectrum usually showed the asymmetrical character indicated in Fig. 12,

<sup>16</sup> Y. Cauchois, J. phys. radium 16, 253 (1955).



but occasionally on the "tail" several weak "bumps" occurred. They are indicated in the figure by dashed lines. Because these loss lines were very weak the accuracy of their measurement was correspondingly less than for the other losses. There were five of these losses. One at 9.6 ev could be due to the second transition in the ionized atom at 9.0 ev. A second loss at 11.8 ev could be correlated with forbidden transitions of 11.3 and 11.4 ev in the ionized atom while a fourth loss of 14.4 ev could be due to the sum of the strong 6.7- and 7.9-ev losses (total 14.6 ev). The third and fifth weak losses were at 12.4 and 16.3 ev and could be attributed to two transitions of each of the two strong losses respectively. (These would give approximately 12 and 16 ev.) However, because these five weak losses are questionable, we have shown in Table VIII only the two strong losses and the 33-ev loss.

### 5. Lead

From the energy-loss spectrum shown in Fig. 12, we see that there is a loss occurring 1.3 ev below the strongest loss line. To explain this loss we postulate an

TABLE VIII. Energy losses of 20-kev electrons in antimony vapor. The column headings are the same as for Table I. The last line represents the inner-shell excitation.

Neutral atom $6^3P_0$ to	Ionized atom $5^3P_0$ to	Excited level (ev)	Energy loss (ev)
$6^4P_{5/2}$		6.0	6.7
$7^4P_{5/2}$		7.9	7.9
	$5^3D_1^0$	8.2	
$4d^{10} 5s^2 5p^3 \rightarrow 4d^9 5s^2 5p^4$			33

intermediate step. The ground state of the neutral lead atom is  $6s^2 6p^2 ^3P_0$ . We assume that we first have the transition  $6^3P_0 \rightarrow 6^3P_1$  taking place. Then the 4.3-ev loss can be explained as being due to the transition of the excited electron from the  $6^3P_1$  level to the  $6^3D_2^0$  level (equal to 4.7 ev). The other losses, with the exception of the 12.4- and 20.3-ev losses, appear to be due to the superposition of two losses resulting from a dipole and an optically forbidden transition respectively. The 5.6-ev loss can be correlated with the average of the losses resulting from the transitions  $6^3P_0 \rightarrow 6^3D_1^0$  and  $6^3P_0 \rightarrow 7^3P_0$  in the neutral atom, while the 8.9-ev loss is the average of the transitions  $6^2P_{3/2}^0 \rightarrow 6^2D_{3/2}$  and  $6^2P_{3/2}^0 \rightarrow 7^2P_{3/2}$  in the ionized atom. The losses at 11.2 and 18.1 ev can then be due to twice the above two losses, or to the sums of the dipole and forbidden transitions. It is also possible that the optically forbidden transition in the ionized atom,  $6^2P_{3/2}^0 \rightarrow 5^2F_{3/2}$  = 11.5 ev, may contribute to the 11.2-ev loss.

The energy loss at 12.4 ev cannot be definitely accounted for. The third dipole transition and a forbidden transition in the ionized atom are of the right order of magnitude, being 12.9 and 12.8 ev, respec-

TABLE IX. Energy losses of 20-kev electrons in lead vapor. The column headings are the same as for Table VIII.

Neutral atom $6^3P_0$ to	Ionized atom $6^2P_{3/2}^0$ to	Excited level (ev)	Energy loss (ev)
$6^3P_1 \rightarrow 6^3D_2^0$		4.7	4.3
$6^3D_1^0$		5.7	5.6
$7^3P_0$		5.5	
	$6^2D_{3/2}$	8.6	
	$7^2P_{3/2}^0$	9.2	8.9
$2 \times (6^3D_1^0)$		11.4	11.2
$2 \times (7^3P_0)$		11.0	
$6^3D_1 + 7^3P_0$		11.2	
	$5^2F_{5/2}^0$	11.5	12.4
	$6^2F_{5/2}^0$	12.8	
	$8^2D_{3/2}$	12.9	
	$2 \times (6^2D_{3/2})$	17.2	
	$2 \times (7^2P_{3/2}^0)$	18.4	18.1
	$6^2D_{3/2} + 7^2P_{3/2}^0$	17.8	20.3
$5d^{10} 6s^2 6p^2 \rightarrow 5d^9 6s^2 6p^3$			

tively. Another possible explanation is that it is due to energy loss in the residual air in the vacuum chamber, as explained earlier. The loss of 20.3 ev is attributed to inner-shell excitation. The x-ray value for the  $O_{4,6}$  shell is given<sup>17</sup> as 22 ev. This would be an excitation of one of the 5d electrons. These energy losses are given in Table IX.

### 6. Potassium Chloride

The energy losses in KCl vapor were measured to find out how similar they might be to the losses in potassium vapor. It was found that, in general, the energy-loss spectra were the same. The strong resonance loss of 1.7 ev and the following loss at 3.3 ev found in potassium appeared equally strong in the KCl vapor at 1.6 and 3.1 ev. On the other hand, a 5.8-ev loss was found in KCl which was not found in potassium. The following loss of 7.8 ev in potassium occurs in the KCl spectrum at 8.4 ev. Of the next six losses in potassium five were found in the KCl vapor. It is perhaps interesting to note that the losses in KCl between 12.4 and 25.8 ev all lie 0.4 to 0.7 ev lower than the equivalent losses in potassium. In Table X we have listed the energy losses in both potassium and KCl, and in Fig. 13 the energy-loss spectrum of KCl is given.

TABLE X. Energy losses of 20-kev electrons in potassium chloride vapor compared to the energy losses in potassium vapor.

Energy losses (ev)		
KCl		K
1.6		1.7
3.1		3.3
5.8		...
8.4		7.8
12.4		13.0
18.6		19.0
22.3		22.8
23.9		24.6
25.8		26.2
...		28.5

<sup>17</sup> Hill, Church, and Mihelich, Rev. Sci. Instr. 23, 523 (1952).

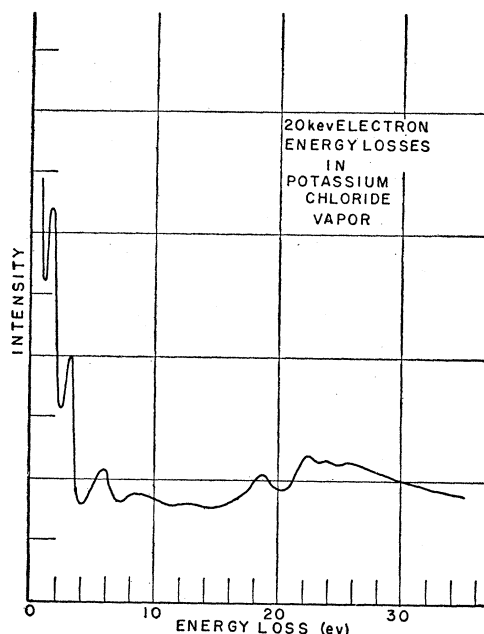


FIG. 13. Energy-loss distribution of 20-keV electrons in potassium chloride vapor. The ordinate is the same as in Fig. 5.

#### REMARKS

The measurements show, as the Born approximation predicts, that dipole excitation does predominate although some optically forbidden excitation does occur, particularly in the high- $Z$  metals. This is especially noticeable in the case of lead where each energy loss results from a combination of a monopole and a dipole excitation.

Our data also verify that the principal interaction is excitation to the first excited level—the resonance excitation. One exception to this rule was found in the case of Sb where the second loss was of equal intensity to the first. This may be due to one of two causes; (1) the loss line was due to two losses, as shown in Table VIII, whose combined intensities brought the intensity of the second loss line equal to the first loss; (2) the

first excitation in the ionized Sb has the same probability as the first excitation in the neutral atom. Our data also show that ionization plays an insignificant role in the spectral distribution as compared to excitation. This is due to the fact that the primary electrons can lose any amount of energy above the ionization potential up to the primary energy in the ionizing process. Therefore, under our measuring conditions, the intensity contribution to the energy-loss spectrum from electrons which have lost energy due to ionization will be spread over an energy range of 20 000 eV. Consequently, we find no rise in the background intensity of the energy-loss distribution as we approach the ionization potential such as one might expect to observe when working with much lower primary energies.

The transitions corresponding to the measured energy losses are in many cases fairly easily established. A number of the energy losses could only be explained on the basis that the incident electron had caused two or three distinctly different transitions, or two or three transitions of the same kind in its traversal of the vapor. Since we were measuring the energy losses in a small solid angle in the zero direction, we had no way of distinguishing the forbidden and dipole transitions. It would be of great interest to measure the energy losses in metal vapors as a function of angle in an effort to separate the forbidden and dipole excitations.

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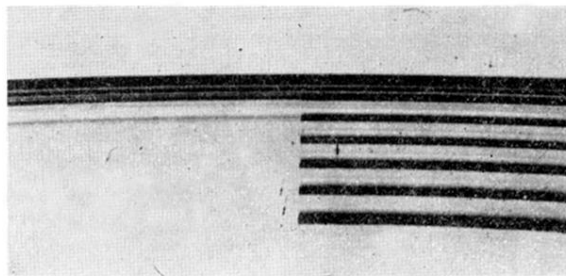


FIG. 3. Photograph of the calcium energy-loss spectrum. The series of equally spaced lines on the right are the 6-volt calibration markers, and the lines on the left represent the energy losses with the uppermost line the zero loss line.