

Electron Characteristic Energy Losses in Metals and Compounds*

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The characteristic energy loss spectra of electrons in the metals Al, C, Sb, Ca, Pb, Na, and Te and compounds of these metals have been measured with an improved measuring technique designed to give more reliable intensity relationships, and it is found that, with the exception of Al_2O_3 , the compound spectra show a decided similarity to the spectra of their parent metal spectra. Rudberg's premise that such a similarity is due to oxidation of the parent metal is shown not to hold. It is proposed that the characteristic losses, except in the case of Al, and possibly Be and Mg, are due to interband transitions. For Al, and possibly Be and Mg, the characteristic losses may be due to excitation of a free electron plasma.

INTRODUCTION

IN 1936¹ Rudberg measured the characteristic energy losses of low-energy electrons in calcium and barium and the oxides of these metals. It was his conclusion that the distribution curves for the oxides were entirely different from those for the parent metals even though there was a strong resemblance between the spectra, particularly at the higher energy levels. He stated that the peaks which were the same, or nearly the same, were merely due to the fact that the fresh metal oxidized so rapidly that a pure metal spectrum could not be obtained. In a short note² we reported that we had found the characteristic loss spectra to be similar for magnesium, silicon, tellurium, and their oxides and for lead, antimony, and their sulfides. Shortly after, there appeared a paper by Watanabe³ in which the spectra for tin and beryllium and their oxides were given. The energy losses and relative intensities for tin and stannous oxide were found to be exactly the same (the diffraction patterns were measured to verify that the tin was not oxidized when measured). We could not ascertain from the data given whether the beryllium and beryllium oxide spectra could be correlated unless one assumed a rather large shift in energy of the spectrum plus the appearance of new low-lying levels.

Our previous results² were obtained by recording the energy-loss spectra on photographic plates, and, therefore, very little could be deduced concerning the quantitative relationships of the energy-loss peak intensities. The present results were obtained with improved instrumentation designed to give more reliable intensity data. We have measured several of the previous spectra as well as some new ones, and have found that in most cases there is a great similarity of the energy loss spectra of elements and their compounds and, indeed, there are cases where they are almost exactly the same.

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

¹ E. Rudberg, *Phys. Rev.* **50**, 138 (1936).

² L. B. Leder and L. Marton, *Phys. Rev.* **95**, 1345 (1954).

³ H. Watanabe, *J. Phys. Soc. Japan* **9**, 920 (1954).

APPARATUS

The analyzer used for these experiments is a modification⁴ of the Mollenstedt⁵ type which utilizes a cylindrical electrostatic lens. The principle of operation and the modifications have been discussed elsewhere.⁴⁻⁶ However, there have been no design data given for the analyzer lens, and we feel it worthwhile to give here the dimensions of the lens used by us, which were obtained empirically. These are given in Fig. 1. The lens is made up of three disks. The outer two have circular apertures of the same diameter, and are maintained at ground potential; the center electrode has an elongated aperture and it is maintained at the negative accelerating potential of the electron source. The long dimension of the center aperture should be large compared to the small dimension, but for practical reasons we made ours approximately 5.3 times the small dimension.

The detector system consists of a glass window

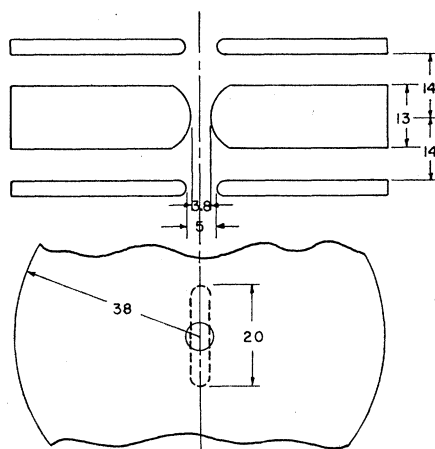


FIG. 1. Dimensional data for the "cylindrical" electrostatic analyzer lens. The electrodes are disk shaped. The outer two electrodes are kept at ground potential while the center electrode is kept at the electron source accelerating potential. Dimensions are given in mm.

⁴ Marton, Leder, and Mendlowitz, *Advances in Electronics Electron Phys.* **7**, 185 (1955).

⁵ G. Mollenstedt, *Optik* **9**, 473 (1952).

⁶ W. Lippert, *Optik* **12**, 467 (1955).

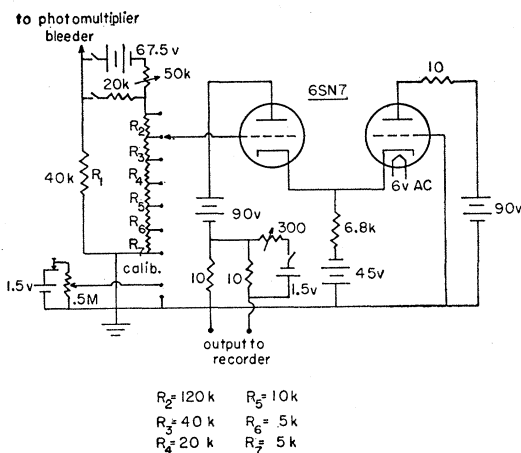


FIG. 2. Impedance matching circuit and range-changing network between photomultiplier and recorder.

coated with P11 phosphor on the vacuum side of the apparatus, and a 1P21 photomultiplier looking into the window from outside the vacuum. The window was made by sealing a microscope cover glass with Epon⁷ into a slit in the vacuum wall. The phosphor-coated edge has the dimension 1.75×0.13 mm while the length of the window is approximately 4.75 mm. Over the phosphor was placed a thin collodion film, and this was then coated with 1600 Å aluminum to keep stray light from entering the photomultiplier.

The output of the photomultiplier is made logarithmic by using a circuit similar to that of Bell and Graham.⁸⁻⁹ This signal is then fed through an impedance matching circuit to a recorder. This circuit, shown in Fig. 2, consists of a range-changing resistor network, connected between the last dynode of the photomultiplier and ground, and a double cathode follower. The signal is taken off at a 20-ohm resistor to match the recorder input impedance. Since the voltage developed across resistor R_1 decreases as the light signal increases, a bucking potential is inserted, as indicated in the figure, to bring the signal on the first grid of the 6SN7, at zero light level, to zero. The recorded voltage is then the difference between the bucking potential and the potential developed across R_1 . There is also included in the circuit a battery and rheostat which can be switched in to give half full-scale reading on the recorder. This, in combination with the zero reading obtained when the first grid is grounded, gives a check on the calibration of the circuit. The calibration was made using a Faraday cage and electrometer.

The scanning of the spectrum is accomplished by using a motor-driven 100 000-ohm ten-turn potentiometer which is across a CK 5651 voltage regulator tube

powered by three 45-volt batteries. The potentiometer is inserted between the lens and high voltage. With this arrangement, the potential on the analyzer is changed continuously over a range of approximately 90 volts, and the energy-loss spectrum moves across the phosphor-coated window. The motor driving the potentiometer rotates at 1 rpm, and the chart drive is 26 mm per minute. The rate of change of potential on the analyzer lens was measured with a Millivac model MV17B voltmeter which was calibrated with a Leeds and Northrup potentiometer. The calibration of the recorder chart was thus found to be 0.37 volt/mm.

EXPERIMENTAL PROCEDURE

The measurements were made with primary electrons of 30–35 keV energy passing through thin films of solids with thicknesses of the order of 200 to 400 Å. Our choice of thin films was limited to the following: (1) those compounds which could be evaporated without decomposition, and (2) those compounds whose oxides could be formed from the evaporated metal film. We were also limited in our mode of measurement by the fact that most of the films were not strong enough to be mounted freely and that many of the metals oxidized very quickly in air. For these reasons all the materials except aluminum, antimony, aluminum oxide, lead hydroxide, lead telluride, lead selenide, and lead sulfide were measured on a Formvar substrate. These were all handled in the same way. A Formvar film was made by putting one drop of a 1% solution of Formvar in ethylene dichloride on a water surface. A piece of the film was then picked up on the specimen holder and allowed to dry over the 0.4-mm aperture. The specimen holder was then placed in the evaporating unit attached to the spectrograph. This unit was prepumped and then opened to the main vacuum. The material to be studied, which had previously been weighed and placed in the tantalum boat of the evaporator, was evaporated onto the Formvar; the entire specimen unit was then placed in position in the beam. By this method we could measure the energy losses in easily oxidized materials several seconds after evaporation without appreciable oxide formation. The freely mounted films were made by evaporation onto a cleaved rock salt surface. They were then floated off on water and picked up on the specimen holder. The lead hydroxide film was made by placing a lead film on the water surface for several minutes. The film quickly lost its metallic color and became clear, indicating full oxidation. It was then picked up on the specimen holder. In the case of aluminum oxide, an aluminum film was first evaporated onto a microscope slide. This film was anodized¹⁰ and stripped from the glass onto a water surface. It was then mounted in the same manner as the other films.

Previous to measurement, the equipment was turned on and allowed to stabilize for at least one hour. The

⁷ Epon is the trade name of an epoxy resin produced by Shell Chemical Corporation.

⁸ R. E. Bell and R. L. Graham, *Rev. Sci. Instr.* **23**, 301 (1952).

⁹ Marton, Simpson, and McCraw, *Rev. Sci. Instr.* **26**, 855 (1955).

¹⁰ G. Hass and M. E. McFarland, *J. Appl. Phys.* **21**, 435 (1950).

specimen was introduced into the beam and its position adjusted for maximum output signal. This maximum occurs when the zero-order diffraction spot is directly over the analyzer slit. The spectrum was then measured going from zero energy loss to approximately 50-ev energy loss, at which point the signal level generally approached zero; and then back again to the zero-loss peak by reversing the helipot drive motor. Each spectrum took approximately 6 minutes to obtain and, in general, only two spectral runs were made with each individual film.

RESULTS

Many of the films studied were supported on a Formvar substrate and thereby a background scattering was added to the film's own scattering distribution. This background could not be eliminated merely by

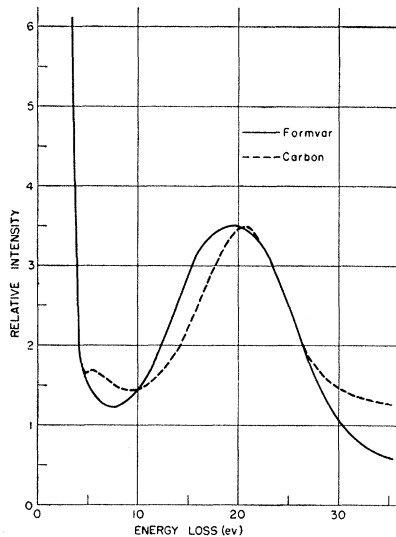


FIG. 3. Energy loss spectra in carbon and Formvar normalized to the peak at ~ 20 ev.

subtracting the Formvar loss distribution—which usually had a higher cross section than that of the film—nor were we able to determine any simple method of correcting the energy-loss distribution for this background. Therefore, in these cases we did not consider it of importance to measure the thickness of the films, which would have to be done if we wished to compare the absolute intensities. Only in the case of aluminum and aluminum oxide, which were both freely mounted, were the thicknesses measured. For this reason the distribution curves are plotted on an intensity scale in arbitrary units of relative intensity. In all cases (except aluminum) we have arbitrarily normalized the curves to the intensity position of one peak. This normalization was done to make it easier to compare the relative heights of the various peaks. We cannot, however, compare intensities between one set of distribution curves and another. The

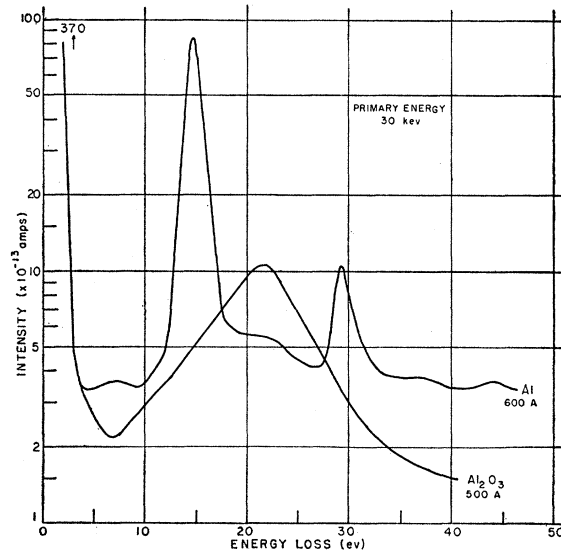


FIG. 4. Energy loss spectra in Al and Al_2O_3 normalized to the intensity of the zero-loss peak. The intensity of this peak is indicated in the upper left-hand corner of the figure.

numerical intensity scale is not completely arbitrary to the extent that we can measure the half-widths (where possible) of the loss lines and bands.

Formvar and Carbon

In Fig. 3 we show the spectra of Formvar (a polyvinyl acetal) and carbon, both of which were free-mounted. These are given to illustrate first what the substrate spectrum looked like, and second, because carbon forms a large component of the Formvar as well as being a possible contaminant on the film surfaces due to the deposition of carbonaceous material where the electron beam strikes. They have very similar spectra consisting of a broad, rather strong, band. Carbon has an additional weak loss at 5.4 ev which is not found for the

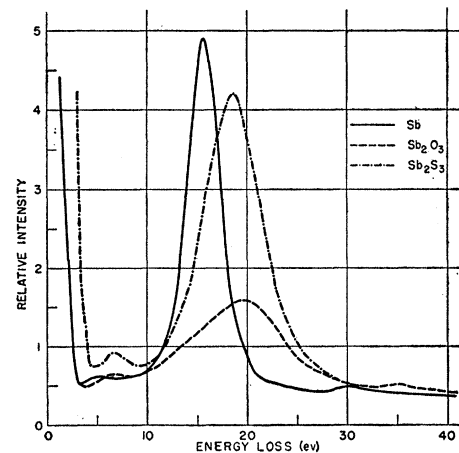


FIG. 5. Energy loss spectra in Sb, Sb_2O_3 , and Sb_2S_3 normalized to the intensity of the third peak.

TABLE I. Energy loss values (in ev) for antimony and its compounds.

Material	Energy loss (ev)		
Sb	5.3	15.6	30.2
Sb ₂ O ₃	6.8	18.6	35.1
Sb ₂ S ₃	6.8	19.9	35.0

Formvar. In the figure the Formvar peak has been normalized to the carbon peak, and we note that the half-width of the carbon peak is approximately 15 ev while that of the Formvar is 1.5 ev broader. When the Formvar is used as a substrate, its energy loss peak does not appear in the superstrate spectrum, but, instead, the entire loss distribution contributes only to the total background scattering.

Aluminum and Aluminum Oxide

These two films were measured without using a substrate. The aluminum thickness was measured with a Tolansky double-beam interferometer¹¹ as being 600 angstroms, while the aluminum oxide thickness was calculated from the initial aluminum thickness of 200 angstroms by the formula,

$$t(\text{Al}_2\text{O}_3) = \left(\frac{M(\text{Al}_2\text{O}_3)}{M(\text{Al})} \right) \left(\frac{\rho(\text{Al})}{\rho(\text{Al}_2\text{O}_3)} \right) t(\text{Al}),$$

to be 500 angstroms. In this formula t is the thickness, M is the atomic and molecular weights, respectively of the aluminum and aluminum oxide, and ρ is the density (assuming that the thin film has the bulk density). Both of these films have been measured by other investigators^{3,12,13} and our measurements are in

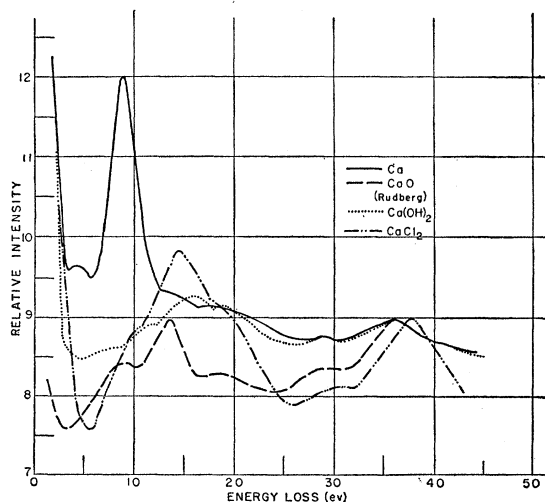


FIG. 6. Energy loss spectra in Ca and some of its compounds. These were all measured on a Formvar substrate (Rudberg measured that of CaO on a silver backing). The curves are normalized to the intensity of the last peak.

¹¹ S. Tolansky, *Multiple-beam Interferometry of Surfaces and Films* (Oxford University Press, London, 1947).

¹² G. Ruthemann, *Ann. Physik* 2, 113 (1948).

¹³ A. Gschlossl, *Physik. Verhand.* 4, 68 (1951).

good agreement with these previous ones. The aluminum spectrum is distinguished by the very strong, narrow 14.6-ev loss and multiples of it. Less frequently observed is the weak 7-ev loss, and combined loss peaks of this one plus those of the 14.6-ev value. The loss spectrum of the oxide differs radically since it consists only of a broad band peaked at 22 ev. The two spectra are given in Fig. 4. They have been plotted on a logarithmic scale because of the wide range of intensities.

Antimony and Compounds

The spectra of the oxide and sulfide look very much like that of antimony with the second of the three losses as the most prominent. The spectra of the two compounds are shifted upward, and show changes in the relative intensities of the peaks as well as in the half width of the main peak. These spectra are shown in Fig. 5. We have plotted them normalized to the intensity of the third maximum. In Table I are listed the energy loss values for these three materials. It should be noted that the values for antimony and antimony trisulfide are somewhat different from those given in

TABLE II. Energy loss values (in ev) for calcium and its compounds. Also listed are the energy loss values for calcium oxide as measured by Rudberg.^a

Material	Energy loss (ev)						
Ca	4.2	8.9	13.2	17.9	...	29.0	36.4
Ca(OH) ₂	...	8.1	11.7	16.0	19.2	29.0	36.2
CaCl ₂	...	10.4	14.6	18.5	...	31.0	37.9
CaO(Rudberg) ^a	...	9.4	13.8	18.3	...	29.0	36.4

^a See reference 1.

our previous publication,² and this is accounted for by improved energy calibration.

Calcium and Compounds

Calcium (Fig. 6) shows six loss peaks with a strong, narrow one at 8.9 ev. The energy loss values are in rather good agreement with those found by Rudberg.¹ The hydroxide of calcium was made by allowing a calcium film to oxidize in air. Actually, it was not determined that the hydroxide rather than the oxide was formed, but only assumed that this was the case. Comparison with the energy loss spectrum for calcium oxide obtained by Rudberg¹ shows several differences, and his spectrum is included in Fig. 8 for comparison. Watanabe³ has also measured the calcium hydroxide energy loss spectrum, and his loss values are in good agreement with ours. The calcium chloride spectrum shows the same intensity structure as that of the hydroxide. Both have a strong peak in the vicinity of 15 ev and another near 37 ev. The strong 8.9-ev loss characteristic of calcium has disappeared in both compounds, but the higher loss peaks can be correlated fairly well. In particular, the last two losses of the

calcium spectrum are both reproduced in the compound spectra. The loss values are given in Table II.

Lead and Compounds

Lead shows three loss peaks with the most prominent at 13.8 ev. The loss spectra for lead sulfide, telluride, and selenide are very similar to that of lead except for small shifts in the first two losses and changes in the relative intensities of the peaks. The loss spectrum for lead hydroxide differs from these in that the first loss has become most prominent and is shifted more than the other compound losses. For all the spectra the loss peak at 21–22 ev remains fixed in position. This loss has been tentatively identified with excitation of electrons from the O_4O_5 shell of lead. In Fig. 7 we show these

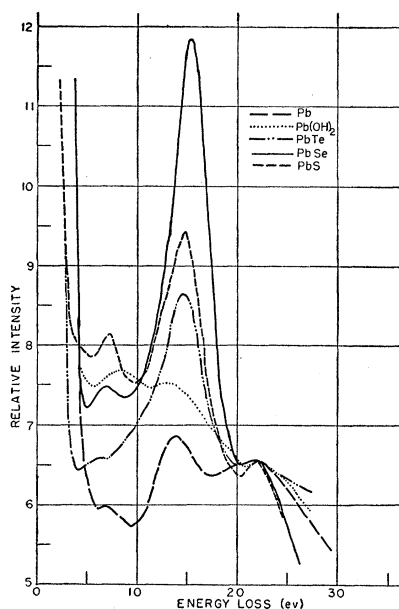


FIG. 7. Energy spectra in Pb and some of its compounds. The Pb spectrum was taken with the Pb on a Formvar substrate. The curves are normalized to the intensity of the last peak.

normalized to the third loss peak intensity. The energy loss values are given in Table III.

Sodium and Compounds

The loss spectra for these materials are given in Fig. 8. The sodium film was approximately 400 angstroms thick, and its spectrum shows five loss peaks. The last loss peak is very weak and somewhat questionable. The first loss is at 5.4 ev and the following ones are in the order of decreasing intensity and multiples of the first loss. The sodium oxide film was made by allowing a sodium film to oxidize in a vacuum of the order of 5×10^{-3} mm Hg for approximately 16 hours (overnight). The film was assumed to be completely oxidized when the metallic-appearing film was replaced by a clear film. The energy loss spectrum of the oxide is not radically different from that of the

TABLE III. Energy loss values (in ev) for lead and compounds of lead.

Material	Energy loss (ev)		
Pb	6.7	13.8	21.4
Pb(OH) ₂	8.4	13.0	22.3
PbS	7.1	14.5	21.8
PbSe	6.9	15.1	22.0
PbTe	6.2	14.4	21.7

TABLE IV. Energy loss values (in ev) for sodium and compounds of sodium.

Material	Energy loss (ev)					
Na	5.5	11.0	16.7	22.1	28.0	...
Na ₂ O	4.5	9.3	14.5	19.7	26.3	...
Na ₂ S	7.2	11.8	17.2	22.2	...	33.4
NaCl	...	9.3	15.9	21.6	...	33.3

metal. The peak positions have shifted downward one to two volts, and the intensity relations of the higher losses have changed so that the third loss peak is slightly stronger than the second or fourth. The first loss remains rather narrow and is still the most prominent just as for the metal. The loss spectra of sodium chloride and sodium sulfide look quite different from that of the sodium, but are similar to each other. The strong 5.4-ev loss of Na has disappeared, and the most prominent peaks now occur at 11.8 ev for sodium sulfide and 15.9 ev for sodium chloride. Although the intensities of the losses are different in these compounds from those in the metal, the loss values still show rather good correlation. These are shown in Table IV.

Tellurium and Compounds

Tellurium (Fig. 9) shows two energy loss peaks. The first is a weak one followed by a strong broad loss

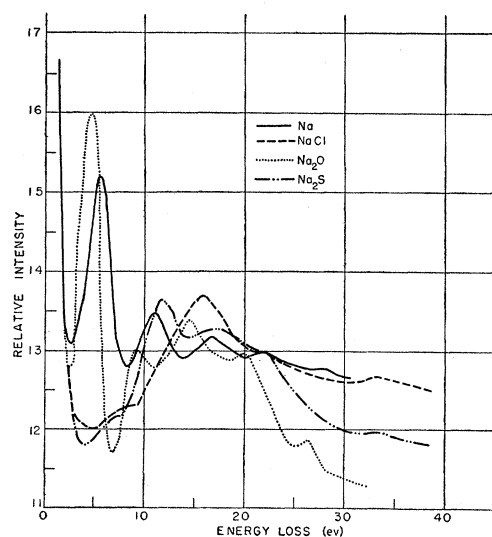


FIG. 8. Energy loss spectra in Na and some of its compounds. These were all measured on a Formvar substrate. The curves are normalized to the intensity of the peak at ~ 22 ev.

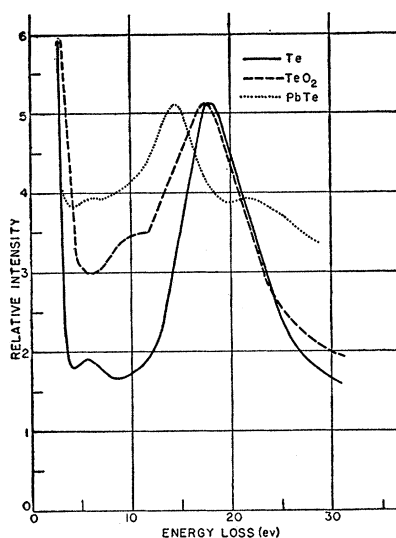


FIG. 9. Energy loss spectra in Te, TeO₂, and PbTe. The Te and TeO₂ films were deposited on a Formvar substrate. The curves are normalized to the intensity of the Te peak at 17.9 ev.

at 18 ev. As in the case of Sb, the loss values are different from our previous values,² and are believed to be more correct. The tellurium dioxide spectrum shows the same structure as tellurium except that the low-lying loss has shifted upward several volts while the main peak has remained fairly constant in energy position but decreased in intensity. On the other hand the lead telluride spectrum shows a different form which was shown to be characteristic of the lead compounds. Since the loss values fall somewhat in the same region for the lead and tellurium spectra, it is difficult to state absolutely that the lead telluride spectrum is determined solely by the lead component; but this view is strengthened by the appearance of the third loss at 22 ev which is a lead characteristic loss. The energy loss values for these materials are shown in Table V.

CONCLUSIONS

All of the metal energy loss spectra that we have measured, with the exception of aluminum, show a decided similarity to the spectra of their compounds. In most cases the differences in the spectra appear to be due to changes in the relative intensities of the energy loss peaks and small shifts in the energy positions of the peaks. We can distinguish, usually, a characteristic form of the metal spectrum carried through to that of the compound. Rudberg's¹ premise that the peaks at approximately 30 and 36 ev in the calcium spectrum are due to the presence of calcium

oxide does not appear to hold true since in the case of sodium, which oxidizes faster than calcium, we do not find the exact duplication of corresponding peak positions and intensities in going from the metal to the oxide; whereas in the cases of antimony, lead, and tellurium, which oxidize much more slowly than calcium in vacuum, and their oxides we still find strong similarities in the spectra. We can conclude from these results that, however the characteristic energy losses may originate in the metal, in most cases compounding appears only to change the relative probabilities of the losses and, to a lesser extent, the loss values themselves. These losses probably arise from interband transitions; and it would then appear that compounding does not introduce radical changes in the energy levels but does alter the densities of states.

The case of aluminum and aluminum oxide can be considered an exception to this general behavior. There is also the possibility³ that beryllium and magnesium may also be exceptions, but until further measurements

TABLE V. Energy loss values (in ev) for tellurium, tellurium dioxide, and lead telluride.

Material	Energy loss (ev)		
	5.6	17.9	...
Te	5.6	17.9	...
TeO ₂	9.9	17.5	...
PbTe	6.2	14.4	21.7

are made of the characteristic energy losses in these metals and their compounds this cannot be definitely stated. If it should be verified that the compounds of beryllium and magnesium do show a different spectral form from those of the parent metals, then it may be that in aluminum, beryllium, and magnesium one observes what can be considered a free-electron plasma loss. Therefore, in the compounding of these metals the free-electron model would not be valid, and one would expect the loss spectrum to be radically different because the loss mechanism would be different.

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