

Effect of Oxidation on the Characteristic Loss Spectra of Aluminum and Magnesium*

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Measurements of the characteristic electron energy loss spectra of aluminum and magnesium were made (in a reflection experiment) during oxidation of a fresh evaporated layer of either metal. It was found that surface oxidation results in the rapid disappearance of the low-lying energy losses (10.3 ev in aluminum and 7.1 ev in magnesium) and the appearance of modified low-lying losses of 7.1 ev in aluminum and 4.9 ev in magnesium. The general changes in the loss spectra and the particular changes in the spectrum of aluminum were in good agreement with the predictions of Ferrell and Stern.

INTRODUCTION

MEASUREMENTS by the present authors of the characteristic electron energy loss spectra of aluminum¹ and magnesium² have shown that the loss spectrum of each element consists of combinations of two elementary energy losses, 10.3 and 15.3 ev in aluminum and 7.1 and 10.6 ev in magnesium. The larger elementary loss in each material has been identified with the bulk plasma loss proposed by Bohm and Pines³ (predicted to occur at $\hbar\omega_p$, where ω_p is the plasma frequency), and the smaller low-lying loss with the lowered plasma loss proposed by Ritchie⁴ (predicted to occur at $\hbar\omega_p/\sqrt{2}$). These conclusions were supported by observations of the energy losses in aluminum-magnesium alloys.⁵

Stern and Ferrell⁶ have recently investigated theoretically the origin of the lowered plasma loss in greater detail, and find that this loss results from excitation of a surface plasma oscillation in which part of the restoring electric field extends beyond the specimen boundary, in contrast to the bulk plasma oscillation in which essentially none of the restoring field extends outside the specimen. The surface plasma oscillation can, therefore, be affected by the presence of any films or contaminants on the specimen surface. Ferrell and Stern find in particular that the presence of a thin layer of oxide on an aluminum surface should lead to the disappearance of the lowered plasma loss at $\hbar\omega_p/\sqrt{2}$, and to the appearance of a modified low-lying loss at about 6.5 ev which should rise to a maximum intensity

approximately 40% of that of the $\hbar\omega_p/\sqrt{2}$ loss in unoxidized aluminum.

The present paper reports measurements made to check the predictions of Ferrell and Stern by observation of the characteristic loss spectra of aluminum and magnesium as oxidation of an initially clean metal surface proceeded.

EXPERIMENTAL PROCEDURE

The electron energy spectra were obtained with the 127° electrostatic electron spectrometer and associated apparatus, employing the reflection arrangement previously described.^{1,2} A primary electron energy of 750 ev was used throughout, as it had been found that the low-lying loss is more prominent under these conditions than with higher primary energies, and hence its behavior could be studied more easily.

The specimen films were prepared by the rapid evaporation of spectrographically pure aluminum and magnesium from tungsten heaters, as before, onto a substrate at room temperature. The pressure in the target chamber was generally less than 5×10^{-6} mm Hg,

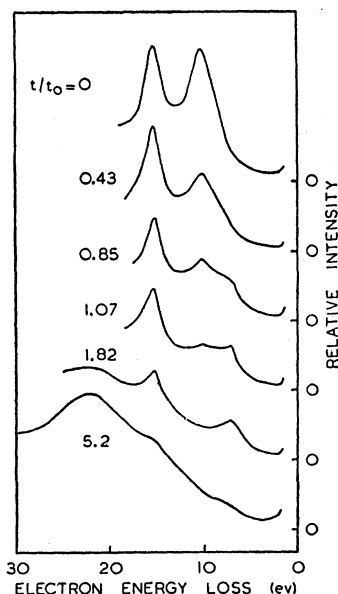


FIG. 1. Portions of the characteristic loss spectra of aluminum in progressive stages of oxidation. The number against each curve is the average value of t/t_0 , where t was the elapsed time after evaporation of aluminum and t_0 was the time in which the measured intensity of the plasma loss decreased to half its initial value. All curves are drawn to the same arbitrary linear intensity scale, the zero of which is shown in each case.

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¹ C. J. Powell and J. B. Swan, *Phys. Rev.* **115**, 869 (1959).

² C. J. Powell and J. B. Swan, *Phys. Rev.* **116**, 81 (1959).

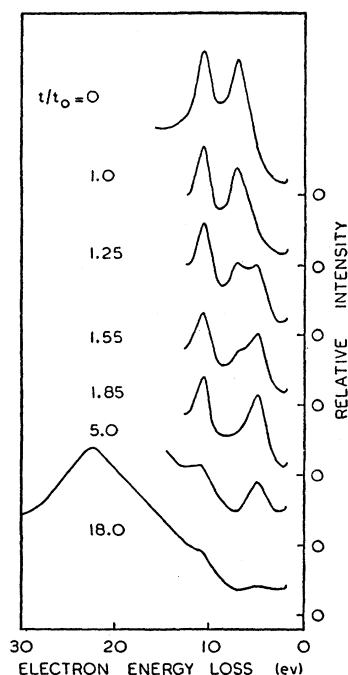
³ D. Pines and D. Bohm, *Phys. Rev.* **85**, 338 (1952); D. Pines, *Revs. Modern Phys.* **28**, 184 (1956); P. Nozières and D. Pines, *Phys. Rev.* **109**, 1062 (1958).

⁴ R. H. Ritchie, *Phys. Rev.* **106**, 874 (1957).

⁵ C. J. Powell, *Aust. J. Phys.* (to be published in June, 1960 issue).

⁶ E. A. Stern, *Bull. Am. Phys. Soc.* **4**, 235 (1959); E. A. Stern and R. A. Ferrell, *Phys. Rev.* (to be published). The authors are indebted to Dr. Stern for communicating some of the theoretical results prior to their publication.

FIG. 2. Portions of the characteristic loss spectra of magnesium in progressive stages of oxidation corresponding to the values of t/t_0 indicated.



though it rose to about 5×10^{-5} mm Hg during evaporations. Immediately after an evaporation, repetitive recording of the loss spectrum of the target in the region of the two elementary energy losses was commenced at a scanning rate of approximately 25 eV per minute. As previous deposits could be covered by the evaporation of a fresh layer of metal, the experiment could be repeated up to about twenty times without opening the vacuum system to recharge the furnaces.

RESULTS

In the absence of any independent identification of the nature of the final surface of the specimen, it has been assumed that the observed changes in the loss spectra with time are primarily, and probably entirely, due to progressive surface oxidation. It was found that the rate at which the changes occurred decreased considerably with frequent evaporations, and it is considered that the gettering action of successive evaporated films reduces the partial pressure of oxygen in the specimen chamber, thus decreasing the rate of oxide formation. It appears likely that similar surface changes in the aluminum or magnesium specimens would have occurred before the measurements could have been made in earlier investigations. Thus, whether or not the specimen changes in the present experiment are due to oxidation, the changes in the loss spectra are significant in that they show a probable source of misinterpretation of the origin of some losses in the past. As the final spectra in the present work are generally similar to the corresponding metal oxide spectra found previously by other workers, however,

the assumption that oxidation predominates appears well founded.

Some typical loss spectra of aluminum and magnesium specimens, in progressive stages of oxidation, are shown in Figs. 1 and 2. It was found that the intensity of the low-lying loss (10.3 eV in aluminum and 7.1 eV in magnesium) decreased rapidly with time, without change in position, and that a new low-lying loss appeared at 7.1 ± 0.1 eV in aluminum and at 4.9 ± 0.1 eV in magnesium. The intensity of this new loss was observed to decrease with time in each case and the spectrum of the target eventually became characteristic of the metal oxide. The spectra of both oxides exhibit a broad prominent energy loss of 22.2 ± 0.1 eV, with a weaker loss peak in magnesium oxide of 39.4 ± 0.4 eV.

The measured relative intensities of the plasma loss, the low-lying loss, and the modified low-lying loss are shown in Figs. 3 and 4 for aluminum and magnesium, respectively, plotted as a function of t/t_0 , where t was the elapsed time after evaporation in each particular series of measurements. A time parameter t_0 was adopted in order to compare the results taken with different oxidation rates, and was defined as the time required for the observed intensity of the plasma loss to decrease to half its initial measured value. The oxidation rate in the present work was generally such that t_0 lay between one and five minutes, its value depending on the initial vacuum obtained before commencing a set of observations and on the number of evaporations prior to any particular observation. In the studies reported previously, where lower pressures and repeated gettering evaporations were employed before spectra were recorded, t_0 was approximately 30 minutes.

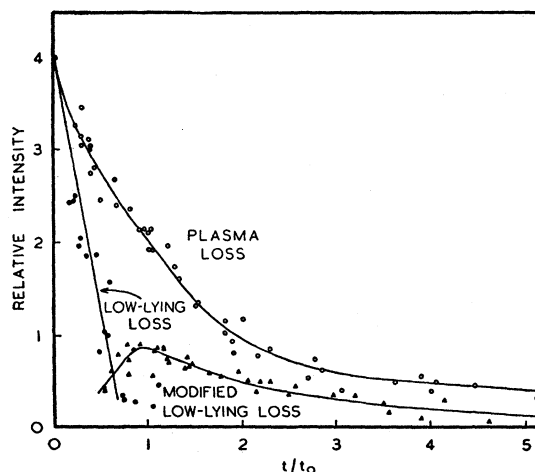


FIG. 3. Intensities of the plasma loss (\circ), the low-lying loss (\bullet), and the modified low-lying loss (\blacktriangle) in aluminum as a function of t/t_0 . Each intensity measurement was made by subtracting an appropriate background from the observed height of the loss peak.

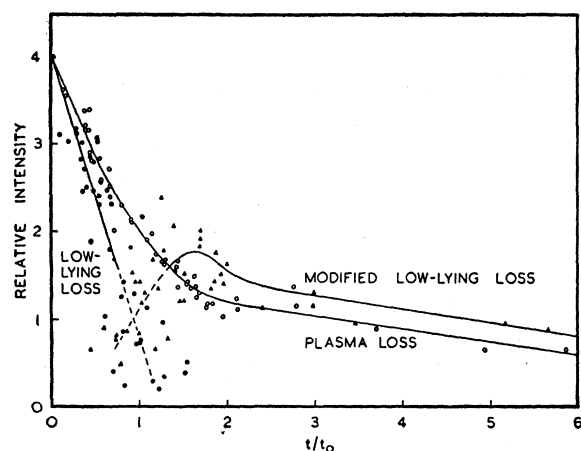


FIG. 4. Intensities of the plasma loss (\circ), the low-lying loss (\bullet), and the modified low-lying loss (\blacktriangle) in magnesium as a function of t/t_0 . The large scatter in the measurements of the low-lying and modified low-lying loss intensities in the vicinity of $t/t_0=1$ results from each peak appearing on a steep background due to the other peak.

As the net electron current to the target was stabilized, changes in the average secondary electron emission coefficient of the target during oxidation would cause variations in the primary bombarding current. Since such current variations are not measurable in the apparatus used, it is not possible to make meaningful comparisons of the measured intensities of any loss at different times. Comparisons of the intensities of any losses at the same time, however, are possible from the curves in Figs. 3 and 4. It should be noted that all peak intensity measurements were subject to errors of the order of 10% because of the uncertainty in location of the background due to inelastic electron scattering and to the generally unknown contribution of the loss spectrum of the oxide.

It may be seen from Figs. 3 and 4 that the original low-lying loss has practically disappeared at $t/t_0=1$, while at about the same stage of oxidation the modified low-lying loss has reached its maximum intensity. As t/t_0 increases, the oxide loss spectrum becomes more prominent and the plasma and modified low-lying loss intensities decrease together at approximately the same rate. The eventual disappearance of the modified low-lying loss indicates that it occurs not in the oxide but in the metal, and then only when a surface layer of oxide is present.

As explained above, comparisons of intensities at different times are not meaningful. However, an indirect comparison of the modified low-lying loss intensity with the initial intensity of the low-lying loss may be made in terms of the plasma loss intensity at subsequent times. Thus the plasma and low-lying loss intensities are approximately equal for a clean surface; for values of $t/t_0 > 1$ the intensity of the modified low-lying loss in aluminum is approximately 45% of the intensity of the plasma loss, implying that it has reached a similar

fraction of the initial low-lying loss intensity in accord with the predictions of Ferrell and Stern. In magnesium, for which no predictions have yet been made, the intensity of the modified low-lying loss exceeds the plasma loss intensity for all $t/t_0 > 1.5$.

DISCUSSION

The above observations verify the earlier conclusion^{1,2} that the low-lying losses in aluminum and magnesium are strongly dependent on the surface state of the specimens. The implicit assumption by many workers that a thin layer of oxide contributes effectively only to the general background has thus been shown to be untenable. Moreover, it is probable that the presence of a substrate in transmission measurements would have a similar modifying effect on the low-lying losses.

Most previous measurements of the characteristic losses in aluminum and magnesium have been made using the transmission technique, the specimen foils usually being prepared by vacuum evaporation onto a substrate either in the analyzer or in a separate unit. The results of the present work show that, quite apart from any effects caused by the substrate, the loss spectra would be severely modified by surface oxidation within a time for which $t/t_0=1$. Without preliminary gettering the parameter t_0 is about one minute in the present vacuum system. As similar vacuum systems (and residual gas pressures) have been utilized by other workers, it is apparent that oxidation of the specimen sufficient to change the loss spectra would have occurred before reliable measurements could have been made, even where the specimen was prepared in the analyzer vacuum system; such oxidation would be completely unavoidable where the foils were prepared outside the analyzer vacuum system and exposed to the atmosphere in transfer. The 10.3 eV low-lying loss in aluminum has not been reported by any other author. It is believed that the low-lying loss found by other workers, at approximately 7 eV, arises from the presence of surface oxide films. The low-lying loss in magnesium observed by Kleinn⁷ at 4.7 eV is similarly considered to be due to the presence of oxide, particularly as the broad oxide loss at 22.1 eV in his spectrum is more prominent than the sharper losses now interpreted as plasma and modified low-lying losses. Gornyi⁸ has observed losses at 4.5 and 7.5 eV in magnesium in a reflection type experiment with primary electron energies between 30 and 100 eV; the 7.5-eV loss may now be interpreted as the low-lying loss and the 4.5-eV loss is believed to be a modified low-lying loss due to the presence of a surface layer of oxide. The magnesium spectra of both Kleinn and Gornyi are similar in appearance to intermediate spectra in Fig. 2.

The energy losses observed by previous workers in

⁷ W. Kleinn, *Optik* **11**, 226 (1954).

⁸ N. B. Gornyi, *Izvest. Akad. Nauk. S.S.S.R. Ser. Fiz.* **22**, 475 (1958).

TABLE I. Published values of the characteristic electron energy losses in aluminum oxide (in ev). The column headings are reference numbers.

9	10	11	12	13	14	15	16
22.31	22.5	22.5	22.5	22	23.0	22	23.7
45.52		45.6	46		46.0		

what are stated to be the oxides of aluminum or magnesium are given in Tables I and II.⁸⁻¹⁷ The prominent loss of 22.2 ev observed for both the oxides in the present work agrees well with other measurements. The losses of 6.9 and 11.7 ev observed by Rudberg in magnesium oxide were stated by him to be doubtful, as the oxide specimens were often thin and nonuniform, and as these losses coincided with those observed with the platinum backing alone. One or two losses between 4.5 and 5.5 ev have been observed by Jull, Watanabe, and Gornyi. Watanabe considered that the loss of about 5.5 ev observed by him represents a localized level in the first forbidden band. Although he states that electron diffraction measurements show complete oxidation, it is not clear that the diffraction examinations were made before the energy loss measurements. It is possible, therefore, that Watanabe's specimens may have been incompletely oxidized at the

TABLE II. Published values of the characteristic electron energy losses in magnesium oxide (in ev). The column headings are reference numbers.

8	12	14	17
5.0	4.5		
6.5	5.5		
10	11.4	5.0	6.9
13		12.0	11.7
18.5			17.5
25	25	22.5	22.7
			33.8

time of measurement and that the 5.5 ev loss could be a modified low-lying magnesium loss.

CONCLUSION

It has been shown that surface oxidation leads to the disappearance of the low-lying energy losses of 10.3 ev in aluminum and 7.1 ev in magnesium, and to the appearance of modified low-lying losses of 7.1 ev and 4.9 ev, respectively. The changes in the energy losses and the loss intensities in aluminum are in good agreement with the theoretical predictions of Ferrell and Stern. It appears that many previous measurements of characteristic losses in aluminum and magnesium have been affected adversely by surface oxidation, and the present observations again emphasize the necessity for clean unoxidized surfaces in this type of work.

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⁹ G. Ruthemann, *Ann. phys.* **6**, 113 (1948).

¹⁰ G. Mollenstedt, *Optik* **5**, 499 (1949).

¹¹ A. Gschlossl, *Physik Verhandl.* **4**, 68 (1951).

¹² H. Watanabe, *J. Phys. Soc. Japan* **9**, 920 (1954); *Phys. Rev.* **95**, 1684 (1954).

¹³ J. A. Simpson, T. F. McCraw, and L. Marton, *Phys. Rev.* **104**, 64 (1956).

¹⁴ G. W. Jull, *Proc. Phys. Soc. (London)* **B69**, 1237 (1956).

¹⁵ L. B. Leder, *Phys. Rev.* **103**, 1721 (1956).

¹⁶ G. Haberstroh, *Z. Physik* **145**, 20 (1956).

¹⁷ E. Rudberg, *Proc. Roy. Soc. (London)* **A127**, 111 (1930).