Origin of the Characteristic Electron Energy Losses in Aluminum*

C. J. POWELL AND J. B. SWAN
Department of Physics, University of Western Australia, Nedlands, Western Australia
(Received March 30, 1959)

The characteristic electron energy loss spectrum of aluminum has been measured by analyzing the energy distribution of 760-, 1000-, 1520-, and 2020-ev electrons scattered by an evaporated specimen through 90°. Twelve loss peaks were observed, made up of combinations of elementary 10.3- and 15.3-ev losses. The former, the low-lying loss, is identified with the lowered plasma loss proposed by Ritchie, and the latter with the plasma loss proposed by Bohm and Pines and previously observed by many other workers. In measurements made with very thin evaporated targets, it was found that the low-lying loss changed considerably in position, as well as in intensity relative to the 15.3-ev loss. These changes, which are interpreted in terms of Ritchie's theory, definitely indicate that the low-lying loss is influenced by the surface layers of the specimen. As targets of high surface and volume purity could be prepared, it is concluded that results obtained by the present reflection technique, when examining loss behavior affected by surface phenomena, are superior to measurements of the characteristic loss spectrum of electrons transmitted through thin films.

SUMMARY OF PREVIOUS WORK

THE first systematic measurements of characteristic electron energy losses were carried out by Rudberg[1] who analyzed the energy distribution of 50–400 ev electrons scattered from the surfaces of a number of metals. In each energy distribution he found peaks which occurred at fixed energy displacements from the peak of elastically scattered electrons, irrespective of the primary bombarding energy or the scattering angle. These peaks therefore corresponded to electrons which had lost definite amounts of energy in the material. Rudberg and Slater[2] proposed that the energy losses were due to excitation of conduction electrons to higher allowed energy levels, and calculated the form of the characteristic loss spectrum of copper, in fair agreement with Rudberg's results.

Ruthemann[3] was the first to extend the measurements to the energy analysis of electrons transmitted through thin films of various materials. Since then, nearly all of the published work has been concerned with the latter type of measurement, and in this paper the two techniques will be referred to as reflection and transmission experiments, respectively.

A large number of workers[4–26] has investigated the characteristic electron energy loss spectrum of aluminum, and the published loss values are shown in Table I. These results of energy analysis of the scattered electron beam have been obtained by using one or other of the following experimental techniques: (a) deflection by electric[4,16] or magnetic[5,6,17] fields with or without prior deceleration; (b) chromatic aberration effects of an electron lens[7–15]; (c) the retarding potential method with electrical[18,19] or numerical[20–23] differentiation. It may be seen that the loss spectrum is made up of combinations of ~15-ev and ~7-ev losses, though the various reported loss values differ considerably.

There have been a number of attempts to explain the origin of the loss lines in aluminum and other materials. Cauchois,[27] Watanabe[8] and Leder, Mendlowitz, and Marton[24] have revived the suggestion of Rudberg and Slater that the energy losses might be due to interband electronic transitions. If this were so, one might expect to find some similarity between the characteristic losses and the absorption maxima found on the short-wavelength side of the various x-ray absorption edges. The comparison is rendered difficult due to the differing electronic states before excitation, which lead to different transition probabilities and line shapes in the two cases. Leder *et al.*[24] made such a comparison for a number of materials and found a fair degree of correlation between the loss values and the displacements of the absorption maxima from the *K*-edges, as well as an indication of a dependence of the former on the inverse square of the lattice constant

* Work supported by the Research Grants Committee of the University of Western Australia.

[1] E. Rudberg, Proc. Roy. Soc. (London) **A127**, 111 (1930); Phys. Rev. **50**, 138 (1936).
[2] E. Rudberg and J. C. Slater, Phys. Rev. **50**, 150 (1936).
[3] G. Ruthemann, Ann. phys. **6**, 113 (1948).
[4] G. W. Jull, Proc. Phys. Soc. (London) **B69**, 1237 (1956).
[5] W. Lang, Optik **3**, 233 (1948).
[6] Simpson, McCraw, and Marton, Phys. Rev. **104**, 64 (1956).
[7] G. Mollenstedt, Optik **5**, 499 (1949).
[8] H. Watanabe, J. Phys. Soc. Japan **9**, 920 (1954); **10**, 321 (1955); **11**, 112 (1956).
[9] W. Kleinn, Optik **11**, 226 (1954).
[10] L. Marton and L. B. Leder, Phys. Rev. **94**, 203 (1954).
[11] B. Gauthé, Compt. rend. **239**, 399 (1954).
[12] F. Leonhard, Z. Naturforsch. **9a**, 1019 (1954).
[13] C. Fert and F. Pradal, Compt. rend. **246**, 252 (1958).
[14] V. I. Milyutin and A. I. Kabanov, Uspekhi Fiz. Nauk, **61**, 673 (1957).
[15] L. B. Leder, Phys. Rev. **103**, 1721 (1956).
[16] Blackstock, Ritchie, and Birkhoff, Phys. Rev. **100**, 1078 (1955).
[17] L. Marton and J. A. Simpson, Rev. Sci. Instr. **29**, 567 (1958).
[18] L. B. Leder and J. A. Simpson, Rev. Sci. Instr. **29**, 571 (1958).
[19] L. B. Leder and L. Marton, Phys. Rev. **112**, 341 (1958).
[20] G. Haberstroh and H. Raether, Naturwissenschaften **42**, 531 (1955).
[21] G. Haberstroh, Z. Physik **145**, 20 (1956).
[22] G. Meyer, Z. Physik **148**, 61 (1957).
[23] H. Boersch, Z. Physik **139**, 115 (1954).
[24] Leder, Mendlowitz, and Marton, Phys. Rev. **101**, 1460 (1956).
[25] Marton, Simpson, Suddeth, Wagner, and Watanabe, Phys. Rev. **110**, 1057 (1958).
[26] A. Gschlossl, Physik. Verhandl. 4, 68 (1951).
[27] Y. Cauchois, Acta Cryst. **5**, 351 (1952).

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

3	4	5	6	7	8	9	10	11	13	14	15	16	18	19	20	21	22	23	25	26
(7)	7.0			7 9	6.5	6.8	6.2		7.8	6.8	7		7.5			(7)		8.7	6.3	7.2
14.72	14.6	14.5	15	15 18	14.8	14.9	13.9	16.5	15.8	15.8	14.6	14.8	15.0	15.0 15.3	15.0	15.2	14.7	14.9	15.3	14.6
	20.5			22	23	21.9	19.2		23.5	22.5	22		22							22
29.59	29.2	29.4		36	29.6	30	27.8		31.6	30	29.2	30.0	30		29.4	30.6		29.8		29.5
							35.0		39		38									37
44.34	43.8	44.2		54		45.6			47.4	45	44.5	44.2								44.5
									54.6											52
59.34	58.4	58.6							63.2			59.8								59.6
73.84	73.0	75.2							79											74
		90.4																		

in materials of similar structure. A summary of measurements of the displacements of the absorption maxima from the K and L_{23} absorption edges for aluminum is given in Table II.[27–32] It will be seen that there is some degree of correlation between these values and the characteristic loss values shown in Table I.

It is interesting to note here that Tomboulian and Pell[32] report the observation of anomalous x-ray absorption peaks in aluminum deposited by evaporation onto a Zapon support. These peaks were not present in freely supported films nor in the Zapon alone. The anomalous absorption was shown to be due in some manner to a surface contamination of the aluminum foil at the metal-backing interface.

In some materials (Al, Mg, Be), the loss lines are much narrower than might be expected from the widths of the energy bands concerned. Tredgold[33] has indicated qualitatively that the sharp lines and the dispersion of energy loss with scattering angle obtained in these materials[8] can be satisfactorily accounted for.

Sternglass[34] has proposed that the characteristic energy losses can be interpreted in terms of individual atomic ionization and excitation, and has calculated the form of the energy loss spectrum of aluminum in good agreement with the results of Ruthemann[3] and Marton and Leder.[10] It could be expected that similar losses would occur when the material was in the vapor state. A series of measurements of electron energy losses[35] in the vapors of a number of materials (excluding Al) has confirmed the known atomic transitions and has shown no correlation with the energy losses in the solid state.

The plasma oscillation theory of Pines and others[36] has yielded a more satisfactory understanding of the loss mechanism. The energy losses are assumed to be due to collective excitation of the conduction electrons, the magnitude of the elementary loss being given by $\hbar\omega_p=\hbar(4\pi ne^2/m)^{\frac{1}{2}}$, where ω_p is the plasma oscillation frequency and n is the density of free electrons in the material. For aluminum, $\hbar\omega_p=15.8$ ev assuming three free electrons per atom.

Pines has shown that the energy loss ΔE should vary with scattering angle θ in the manner

$$\Delta E=\hbar\omega_p+\frac{3E_0P^2}{5m\hbar\omega_p}\theta^2, \tag{1}$$

where P is the momentum of the incident primary electron and E_0 is the energy of an electron at the top of the Fermi band. This equation neglects the effects of electron exchange and departures from free-electron behavior caused by the positive-ion lattice.[37] The form of the relation, however, has been verified experimentally by Watanabe,[8] Meyer,[22] and Marton[38] for aluminum and a number of other elements.

The plasma theory predicts a maximum energy loss and hence a maximum angle of scattering θ_c given by

$$\theta_c=\hbar k_c/P, \tag{2}$$

where k_c is the cutoff wave number for collective excitation given by Pines as

$$k_c=0.353k_0r_s^{\frac{1}{2}}, \tag{3}$$

where k_0 is the wave number of an electron at the top of the Fermi band and r_s is the average interelectronic spacing in units of the Bohr radius. Taking account of exchange, Ferrell[37] has modified Eq. (3) and finds better agreement with the cutoff angles observed by Watanabe and Meyer. Ferrell[39] has also shown that the differential cross section per valence electron for scattering through an angle $\theta(<\theta_c)$ is given by

$$\sigma(\theta)d\Omega=\left(\frac{d\Omega}{2\pi na_0}\right)\left(\frac{\theta_E}{\theta^2+\theta_E{}^2}\right), \tag{4}$$

[28] A. Sandstrom, Arkiv Mat. Astron. Fysik **28A**, No. 12 (1941).
[29] Munier, Bearden, and Shaw, Phys. Rev. **58**, 537 (1940).
[30] L. Rudstrom, Arkiv Fysik **12**, 287 (1957).
[31] J. E. Johnston, Proc. Cambridge Phil. Soc. **35**, 108 (1939).
[32] D. H. Tomboulian and E. M. Pell, Phys. Rev. **83**, 1196 (1951).
[33] R. H. Tredgold, Physica **22**, 1219 (1956).
[34] E. J. Sternglass, Nature **178**, 1387 (1956).
[35] L. B. Leder, Phys. Rev. **107**, 1569 (1957).
[36] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953), and preceding papers; D. Pines, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 367; D. Pines, Revs. Modern Phys. **28**, 184 (1956); P. Nozières and D. Pines, Phys. Rev. **109**, 1062 (1958); D. Pines, Suppl. Nuovo cimento **7**, 329 (1958).
[37] R. A. Ferrell, Phys. Rev. **107**, 450 (1957); H. Kanazawa and S. Tani, Progr. Theoret. Phys. (Kyoto) **19**, 153 (1958).
[38] L. Marton, Revs. Modern Phys. **28**, 172 (1956).
[39] R. A. Ferrell, Phys. Rev. **101**, 554 (1956).

where θ_E is given by $\hbar\omega_p/2E$, E is the energy of the primary electron, and a_0 is the Bohr radius. Experiment[6] indicates that the loss intensity may decrease more rapidly with angle than suggested by (4).

Gabor[40] has proposed a model for collective excitation applicable to the interaction of electrons with thin films of solids. The theory predicts a nonlinear increase in plasma loss intensity with film thickness as well as suggesting two crucial experimental tests. Jull[4] has shown, however, that the ~15-ev loss intensity in aluminum increases more rapidly with thickness than indicated by Gabor's theory. The discrepancy was considered to be due to the existence of disturbed surface layers which could cause a reduction in the effective film thickness.

Ritchie[41] and Ferrell[42] have criticized Gabor's theory. Ritchie, describing the conduction electrons in a thin film by the hydrodynamical equations of Bloch, has found that the effect of the film boundaries is to cause a decrease in intensity of the plasma loss and the appearance of an additional loss at $\hbar\omega_p/\sqrt{2}$ if the foil can be represented as a plane parallel-sided film, or at $\hbar\omega_p/\sqrt{3}$ if the foil consists of spherical grains. This behavior is attributed to the depolarizing effect of the film or grain boundaries. Ritchie proposed that the low-lying losses observed in many materials (~7 ev in Al) are due to this mechanism and has calculated the probabilities of energy losses at the plasma and lowered plasma frequencies as a function of foil thickness. Marton *et al.*[25] have investigated experimentally the applicability of Ritchie's theory to aluminum, and have concluded that the low-lying loss is not a lowered plasma loss. Though the position of the loss found by them did not agree with the theory, they reported that their measurements of the intensity variations of the ~15-ev loss and the low-lying losses could be made to agree better with the theory if the angular aperture of their detector was taken into account, together with the angular distribution given by the plasma theory. In a recent abstract by Marton's group, Wagner *et al.*[43] conclude that "the preponderance of evidence argues against the hypothesis of surface polarization causing the low-lying losses."

Ferrell *et al.*[44] have considered that the ~7-ev loss in aluminum might be due to a band-band transition and have shown that, if this were so, the transition probability would be 0.7% of the plasma excitation probability. They concluded that the loss might be due to carbonaceous contamination on the surface of the specimen.[45]

TABLE II. Displacements of the absorption maxima from the K and L_{23} edges in the x-ray absorption spectrum of aluminum (in ev). The column headings are reference numbers.

K edge				L_{23} edge	
27	28	29	30	31	32
6.1	6.0	8.1	6	3.8	6.6
	11.8			10.0	10.0
14.0		13.5	14		16.9
		24.5		23	23.3
	35.8	34.0			32.6
37				39	
		42.0			44.8
55	51.9			54	54.7
74					77.6

A separate determination of the plasma frequency in metals may be made by the measurement of that radiation frequency at which the material becomes transparent.[36] Sabine[46] has shown that the reflectivity of aluminum decreases with wavelength from 2000 A, reaching zero at about 800 A (15.5 ev). Walker, Rustgi, and Weissler[47] have recently measured the reflectivity and transmittivity of unbacked evaporated aluminum films in the soft x-ray region. They find the onset of transparency at 14.6 ev, in fair agreement with the energy loss measurements.

Ferrell[42] has proposed that an excited plasma in a thin film can, under the proper circumstances, lose energy by the emission of a photon of frequency ω_p. Rudberg[48] made an unsuccessful attempt to detect radiation from thick targets and no reports of the detection of radiation emitted in the manner described by Ferrell have yet appeared.

It has not been possible to explain all of the observed characteristic energy losses in terms of plasma excitation. Pines[36] has shown that for small scattering angles plasma excitation should predominate over interband transitions, and considers therefore that the dominant loss in each substance is due to the former mechanism and that any other losses might be due to the latter. He and Sobelman[49] have suggested that the correlation between the x-ray fine structure and the dominant characteristic losses can be explained by plasma excitation.

It has been suggested that the medium with which the primary electrons interact can be represented as a dielectric.[50–52] By considering the frequency dependence

[40] D. Gabor, Phil. Mag. **1**, 1 (1956).
[41] R. H. Ritchie, Phys. Rev. **106**, 874 (1957).
[42] R. A. Ferrell, Phys. Rev. **111**, 1214 (1958).
[43] Wagner, Suddeth, Simpson, and Marton, Bull. Am. Phys. Soc. Ser. II, **4**, 44 (1959).
[44] Lupton, Ferrell, and Myers, Bull. Am. Phys. Soc. Ser. II, **3**, 191 (1958).
[45] As the presence of the more intense, broad 25-ev carbon peak would considerably increase the background under the aluminum peaks in that vicinity, it is considered unlikely by the authors that the ~7-ev loss is due to the carbon alone (in most cases), though it will be shown that such surface contamination may act to modify the low-lying loss.
[46] G. B. Sabine, Phys. Rev. **55**, 1064 (1939).
[47] Walker, Rustgi, and Weissler, Bull. Am. Phys. Soc. Ser. II, **3**, 414 (1958).
[48] E. Rudberg, Proc. Roy. Soc. (London) **A129**, 652 (1930).
[49] I. I. Sobelman and E. L. Feinberg, Zhur. Eksptl. i teoret. Fiz. **34**, 494 (1958).
[50] J. Hubbard, Proc. Phys. Soc. (London) **A68**, 976 (1955).
[51] Marton, Leder, and Mendlowitz, *Advances in Electronics, and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 183.
[52] H. Mendlowitz, Bull. Am. Phys. Soc. Ser. II, **3**, 191 (1958); **4**, 44 (1959).

of the dielectric constant, the electron energy losses may be calculated for metals and insulators. Mendlowitz[52] has recently stated that both the ~7-ev and ~15-ev losses in aluminum can be explained in this manner, and that Ritchie's theory of the origin of the low-lying losses is "untenable."

Experimentally, it has generally been difficult to determine the precise origin of any energy loss because of the lack of knowledge about the electronic structure in the various materials and also because of the fact that often the various theories predict energy losses and relative intensities of about the same value. The lack of optical data in the ultraviolet and soft x-ray regions has also hindered possible identification of the electron energy loss mechanism.

INTRODUCTION TO PRESENT WORK

Other workers have previously found that similar energy losses are observed in both reflection and transmission work. For the primary electron energies used in this experiment, the maximum scattering angles which could result from each plasma excitation would, by (2), be 3–5 degrees, and therefore the electrons reaching the analyzer must also have suffered single or multiple scattering through a large angle (in this case ~90°). It is thus evident that the loss spectrum observed in reflection work gives a representation of the plasma excitation integrated over all plasma scattering angles; i.e., the electron spectrometer has, effectively, a large angular aperture for electrons that have lost energy by plasma excitation.

This paper describes a measurement of the characteristic loss spectrum of aluminum at low primary energies in a reflection type experiment. Reflection work has the advantage that the specimens may generally be more easily prepared with high purity. In the transmission work, the films (of the order of a hundred angstroms in thickness) are usually prepared by vacuum evaporation onto a substrate, and the subsequent electron energy loss determinations are made either with the film on the substrate or with the film stripped from the backing and freely mounted on a suitable holder. The foils are often exposed to air before analysis, leading to unknown surface oxidation and contamination. Though the backing or small layer of oxide may contribute only a negligible amount to the background scattering, it will be shown that the observed loss spectra may be modified considerably. In particular, the present work has been undertaken with specimens of high surface and volume purity in an endeavor to investigate the surface-sensitive properties discussed in the preceding section.

One drawback to the reflection technique is that only the integrated scattering through a large angle can be observed, and scattering probability will vary with angle and electron energy. It does constitute a convenient method, however, for examining the general features of characteristic loss spectra at low primary energies.

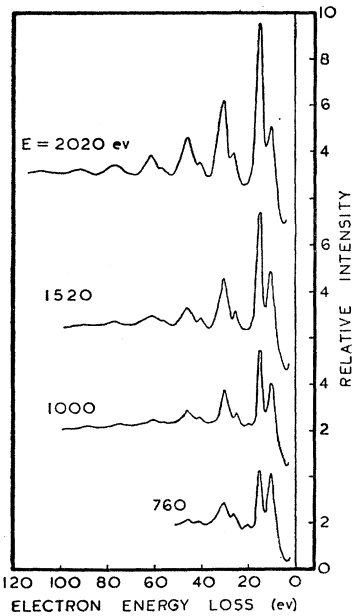

FIG. 1. Characteristic electron energy loss spectra for primary electron energies of 760, 1000, 1520, and 2020 ev. The peak of elastically scattered electrons (not shown) has been adjusted to an intensity of 25 units in each case.

APPARATUS

The 127° electrostatic electron spectrometer is the same as that described previously,[53] except for a replacement of the target chamber. New facilities provide for vacuum evaporation of target material from either of two furnaces onto a tantalum substrate, the plane surface of which is inclined at 45° both to the direction of the incident electron beam and to the direction taken by the scattered electrons entering the spectrometer. Provision is also made for target heating and temperature control, and the target is surrounded by an earthed liquid air trap to reduce the carbonaceous contamination rate and to act as an electrostatic shield. The pressure in the target chamber was normally less than 2×10^{-6} mm Hg, except during evaporations when it was less than 10^{-5} mm Hg.

The spectrometer entrance and exit slit widths were set at 5×10^{-3} in. and a collimating slit, two inches from the entrance slit and set at 15×10^{-3} in., limits the angular divergence of electrons entering the

TABLE III. Measured widths at half maximum intensity of the elastically scattered electron peaks and the 15.3-ev characteristic electron loss peaks for the primary electron energies indicated.

Primary energy (ev)	Elastic peak width (ev)	15.3-ev loss peak width (ev)
769	1.35	2.83
1000	1.62	3.03
1520	1.97	3.24
2020	2.22	3.57

[53] Powell, Robins, and Swan, Phys. Rev. **110**, 657 (1958).

TABLE IV. Measured mean values of the characteristic electron energy losses in aluminum, together with the probable errors and number of measurements associated with each mean. The energy losses and errors are expressed in ev.

Loss value	10.3	15.3	20.5	25.6	30.5	41.1	46.1	56.0	61.4	77.0	91.8	108.6
Probable error	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.2	0.2	0.3	0.3
Number	227	278	50	174	256	89	202	13	115	56	24	5

spectrometer. The target-collimating slit distance is 1.5 in., and all slits are 0.5 in. in length. The width at half maximum intensity of the peak of elastically scattered electrons is given in Table III for each primary energy used, and includes instrumental and primary energy spread effects.

A characteristic loss spectrum can be obtained in a few minutes by using a motor-driven helical potentiometer to continuously vary the spectrometer deflector plate potential difference, and by simultaneously recording on a chart recorder the output of the counting rate meter. Rotation of the potentiometer shaft is converted to an energy loss scale by potentiometric reference to a standard cell.

EXPERIMENTAL PROCEDURE

The target surfaces were prepared by evaporation of spectroscopically pure aluminum from a helical 3-strand tungsten filament, and were believed to be of high volume and surface purity. The evaporation time was purposely made short, a fresh film of estimated thickness 50 to 100 A being deposited in a few seconds; such films were found to give spectra similar to those of thicker films. It was further observed that spectra were not sensitive to substrate temperature during evaporation, and generally both evaporation and scanning were performed at target temperatures of about 200°C.[53]

Several preliminary evaporations of aluminum were used to getter the chamber. The target oxidation and carbonaceous contamination rates were small enough to permit a spectrum to be recorded and then repeated without any significant change taking place. No effects which might be ascribed to evaporation of the tungsten filament or its supports were observable, and while it is possible there may have been a monolayer of adsorbed gas on the target suface, results indicate that the effects of any such contamination are small.

RESULTS AND DISCUSSION

(a) Thick Films

The characteristic electron energy loss spectrum of aluminum was measured for primary electron energies of 760, 1000, 1520, and 2020 ev. The normalized spectra are shown in Fig. 1 with the intensity scales adjusted so that the peak of elastically scattered electrons has an intensity of 25 units in each case. The loss spectrum at 760-ev primary energy is incomplete as it was experimentally inconvenient to extend the energy loss scan at this primary energy. Mean energy loss values are shown in Table IV together with the probable errors and the number of measurements associated with each mean. In agreement with other authors, no significant difference was found in the energy loss values for the different primary energies. No correction has been made for any shift in peak positions due to the background, as the peaks are sharp and the background slowly varying.

It is clear that the loss spectra are composed entirely of combinations of 15.3- and 10.3-ev losses. The former is identified as the ~15-ev plasma loss observed in transmission and the low-lying loss tentatively as the lowered plasma loss proposed by Ritchie.[41] The ratio of these energy losses is then 1.49, slightly greater than the ratio 1.41 predicted by Ritchie. It should be noted here that the latter ratio refers to energy losses in the forward direction, whereas the measured ratio compares the mean energy losses of electrons scattered through all plasma scattering angles. Agglomeration in the target film may also affect the measured ratio, and will be discussed later.

The widths of the 15.3-ev peak at the different primary energies are shown in Table III. This table indicates that, taking into account the spectrometer resolution and the energy spread of the primary electron beam, the width of the plasma line is 1.4 ± 0.1 ev. This width is consistent with the dispersion of the energy loss and the distribution of intensity with plasma scattering angle [Eqs. (1) and (4)].

If it is assumed that the 10.3- and 15.3-ev losses can only be excited in single quantum units and that the probability of excitation per unit distance traveled in the specimen is constant over the total path in the specimen, then it can be shown that the probability of occurrence of an energy loss involving m quanta of the 10.3-ev loss and n quanta of the 15.3-ev loss is given by

$$P_{10.3m+15.3n}(d) \propto \frac{1}{(m+n)!}\left(\frac{d}{\lambda_{10}}\right)^m e^{-d/\lambda_{10}}\left(\frac{d}{\lambda_{15}}\right)^n e^{-d/\lambda_{15}}, \quad (5)$$

where d is the average distance traveled by an electron in the target and λ_{10} and λ_{15} are the mean free paths for the 10.3- and 15.3-ev losses, respectively, for a given primary energy. From this relation it is possible to determine the relative probabilities of the various losses and, by comparing these with the areas under the appropriate peaks, a number of independent values of the ratios d/λ_{10} and d/λ_{15} can be obtained for each primary energy. However, as no background could be

drawn which would give, for a particular primary energy, consistent values of both d/λ_{10} and d/λ_{15}, it was therefore concluded that the simple assumptions were incorrect. Further analysis of the observed spectra indicated that the probability of a 10.3-ev loss may be higher, and the probability of a 15.3-ev loss is lower, in the vicinity of the target surface. This conclusion is in agreement with the predictions of Ritchie.

It can be seen from Fig. 1 that the ratio of intensities of the 15.3- and 10.3-ev losses changes considerably with primary electron energy. Ritchie has calculated the relative probabilities of the plasma and lowered plasma losses in a thin film (of thickness a) as a function of the parameter $t=a\omega_p/v$, where v is the primary electron velocity. If a is replaced by d, the average electron path length, and this is assumed to vary with primary energy in the manner indicated by the work of Young,[54] the present results qualitatively verify Ritchie's calculations.

(b) Thin Films

To investigate further the theories of Gabor and Ritchie, measurements were made of the characteristic loss spectra of much thinner films. These were prepared by evaporation of a known mass of aluminum onto the target, the substrate generally being a layer of carbonaceous contamination. As before, several evaporations of aluminum were carried out from one furnace (with the target suitably shielded) prior to the evaporation of the known mass from the other furnace. As it was easier to handle, aluminum of commercial purity was used here, for it had previously been shown that this gave results identical to those of the spectroscopically pure material.

The average thickness of each deposit was calculated assuming isotropic evaporation and total condensation on the target. The latter assumption would appear to be justified in view of the results of Chandra and Scott[55] and the fact that no reflected deposits of aluminum were seen on the inside of the cold-trap. It is realized that the average thickness calculated in this way may be in considerable error; the results, however, are internally consistent and are indicative of the loss behavior for small thicknesses.

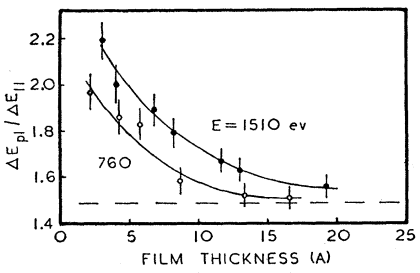

FIG. 2. The ratio ($\Delta E_{pl}/\Delta E_{ll}$) of the plasma (15.3 ev) loss to the low-lying loss as a function of average film thickness for primary electron energies of 760 and 1510 ev. The dashed line corresponds to the measured value of this ratio for much thicker films.

As mentioned earlier, Ritchie has stated that the low-lying loss should occur at $\hbar\omega_p/\sqrt{2}$ for a plane parallel-sided film or at $\hbar\omega_p/\sqrt{3}$ for a film of spherical grains. This former predicted behavior is generally verified as, for a thick film, the loss occurs at $\Delta E_{pl}/1.49$, where ΔE_{pl} is the measured value of the plasma energy loss. As the average film thickness was decreased, it was observed that the plasma loss remained at the same position (ΔE_{pl}) but the position of the low-lying loss peak (ΔE_{ll}) changed to smaller energy loss values. In Fig. 2, the ratio $\Delta E_{pl}/\Delta E_{ll}$ is plotted against estimated average film thickness for primary electron energies of 760 and 1510 ev. Agglomeration would be expected to become much more pronounced in these thin films, and to shift the low-lying loss in the manner observed. It may be seen that for the thinner films ΔE_{ll} decreases to a value less than $\hbar\omega_p/\sqrt{3}$. At such thicknesses, the loss spectrum of the substrate predominates over that of the aluminum and it is conceivable that the extra shift might be due in some manner to the substrate. Though the plasma loss is unchanged in position (thereby proving that the volume purity of the aluminum is not changed), the aluminum-substrate interface may, in effect, contaminate the aluminum surface. As in the transmission experiments, such surface contamination is possibly the cause of part of the observed shift. It is important to note, however, that in the case of the thick films the low-lying loss is observed near its predicted position.

It is interesting to determine the minimum film thickness at which the loss spectrum is characteristic of a thicker specimen. It is seen from Fig. 2 that this minimum is 15–20 A for a primary energy of 760 ev and 25–30 A for a primary energy of 1510 ev. The average electron path length in the material would reasonably be expected to be about twice this distance, and this estimate, together with the estimate for the mean free path for plasma excitation, agrees with approximate calculations of d/λ_{15}.

Measurements have also been made on the plasma and low-lying loss intensities as a function of average film thickness; these measurements were subject to considerable error as it was difficult to locate the background, which includes an unknown contribution from the substrate. Nevertheless, the results are interesting in that they are again consistent and do indicate the following trend of the intensity changes. For the two primary energies concerned, the plasma and low-lying loss intensities were seen to increase nearly linearly with average film thickness, approaching a maximum at the same value of film thickness as that for which the low-lying loss approached its thick-film position. The ratio of the low-lying loss intensity to that of the plasma loss was, however, seen to increase

[54] J. Young, J. Appl. Phys. **27**, 1 (1956).
[55] S. Chandra and G. D. Scott, Can. J. Phys. **36**, 1148 (1958).

significantly as the film thickness decreased, in the manner predicted by Ritchie. It was noted that the maximum peak intensities in the thickest of the thin films investigated (i.e., ~20 A) were slightly different to those observed for much thicker films; similar fluctuations of the peak intensities ($<\pm 5\%$) in the thick films were attributed to differences in structure following slightly different evaporation conditions.[25]

The change in plasma loss intensity with thickness may be of the same form as indicated by Gabor's Q-function (for the appropriate electron energy), but the results are not sufficiently precise for detailed comparison. The change in the low-lying loss intensity may also be slightly nonlinear but with the curvature in the opposite direction, the net result being the change in the ratio of the two intensities just mentioned. The strong nonlinear increase in intensity of the plasma loss with thickness found by Jull with 10-kev primary electrons was not observed.

It is necessary to discuss the likely structure of the evaporated films.[56] For the thicker films (50 to 100 A) and for the rates of evaporation used, the deposits are probably agglomerated to some extent but are definitely continuous, as no electrons scattered by the substrate are detected. As the average film thickness decreases, the films would be expected to become more strongly agglomerated, but are probably continuous down to about 10 A. In future experimental investigations of the theories of Gabor and Ritchie, it would be desirable to use primary electrons of higher energy, in order that agglomeration and structure changes in the target film would be of lesser effect.

CONCLUSION

Experiments of the reflection type are desirable in studies of characteristic electron energy losses involving surface properties, as the targets can be made thick enough to eliminate all possible effects of the support. The present work indicates the necessity of using specimens of high volume and surface purity.

While the transmission technique is useful in work where the scattering angle for characteristic loss excitation needs to be unambiguously known, it has been shown that in this type of experiment there could always be doubt as to the surface purity of the specimen. Even when the specimen has been prepared (on a substrate) and analyzed in the same vacuum, it is probable that the substrate influences the low-lying losses as well as sometimes the main losses,[51] and it is perhaps not surprising that the former have been observed in different positions by different workers.

The results obtained in this work show that the characteristic loss spectrum of thick films of aluminum is made up of component losses of 10.3 and 15.3 ev; the former is associated with the surface layers and the latter with the bulk material.

The observed loss behavior for both thin and thick films may be readily interpreted in terms of Ritchie's theory. The change with film thickness in the position and intensity of the low-lying loss, and in the ratio of intensities of the two fundamental components, indicates that the 15.3-ev loss arises from plasma excitation and that the low-lying loss is a lowered plasma loss arising from surface phenomena.

ACKNOWLEDGMENTS

One of us (C.J.P.) wishes to acknowledge the tenure of the Imperial Chemical Industries of Australia and New Zealand Research Fellowship and a Commonwealth Scientific and Industrial Research Organization Senior Postgraduate Studentship at different times during this work.

[56] L. Holland, *Vacuum Deposition of Thin Films* (Chapman and Hall Ltd., London, 1956), pp. 207, 327.