

THE CHARACTERISTIC ELECTRON ENERGY LOSS SPECTRA OF ALUMINIUM-MAGNESIUM AND ALUMINIUM-COPPER ALLOYS

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Summary

The characteristic electron energy loss spectra of 1500 eV electrons scattered by aluminium-magnesium and aluminium-copper alloys have been measured. A plasma and a lowered plasma energy loss were observed in the alloys, and it was found that surface oxidation caused the disappearance of the lowered plasma loss and the appearance of a new modified lowered plasma loss. Though the compositions of the evaporated alloy specimens were unknown, the three energy losses were observed to vary continuously between the values observed for the three elements. This continuous change can be interpreted in terms of the changing free electron density in alloys of varying composition. It is concluded that measurements of the characteristic loss spectra of alloys can differentiate between losses due to individual and collective electron excitation.

I. INTRODUCTION

In a previous paper, possible reasons for the many discrepancies in the measurements of characteristic electron energy losses in solids by different workers have been discussed (Powell 1960*b*). New measurements in this laboratory have shown the source of some of these discrepancies and have enabled positive identification of the origin of many energy losses to be made. Before that work was carried out, however, it had been considered that an experiment which could be useful in determining the energy loss mechanism would be the measurement of the energy loss spectra of certain metal alloys.

It had been proposed that the dominant energy loss in a metal was due to the collective excitation of the conduction electrons (Pines 1956; Nozières and Pines 1958, 1959). For a free-electron gas, the energy loss is $\hbar\omega_p = \hbar(4\pi ne^2/m)^{1/2}$, where ω_p is the free-electron plasma frequency and n is the density of free electrons. Where the conduction electrons in a metal are weakly bound and the outermost core electrons strongly bound, the observed energy loss would be expected to be close to $\hbar\omega_p$ and the half-width of the loss small compared to $\hbar\omega_p$. In a metal where the binding energies of the valence and outermost core electrons are similar, the observed energy loss would be displaced appreciably from $\hbar\omega_p$ and the half-width of the loss peak would be of the order of $\hbar\omega_p$.

It had also been suggested that many of the energy losses were due to interband electronic transitions. Rudberg and Slater (1936) compared the loss spectrum of copper observed by Rudberg (1936) with one calculated from previous studies of the band structure, with fair agreement. More recently, Cauchois

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(1952), Watanabe (1954, 1956), and Leder, Mendlowitz, and Marton (1956) compared the energy losses observed in a number of elements with the displacements of subsidiary absorption maxima from the K and L edges in the X-ray absorption spectra. These authors found a degree of correlation between the loss values and the fine-structure displacements, and Leder, Mendlowitz, and Marton found some dependence of the energy losses on the inverse square of the lattice constant in elements of similar structure. Viatskin (1958) has also found fair agreement between some observed energy losses and values calculated using the interband transition hypothesis.

Measurements of the loss spectra of binary alloys of varying composition might therefore differentiate between these two mechanisms for the origin of a particular energy loss. If the dominant energy losses in two elements were due to plasma excitation, one might expect that a gradual shift in the energy loss with changing electron density would be observed in the alloy spectra. Alternatively, if the losses were due to interband transitions, it might be expected that the losses due to one element would gradually decrease in intensity while the losses characteristic of the second element gradually increased in intensity in alloys of increasing content of the second element, with possibly a small variation in each loss position caused by band structure changes. Alloys of aluminium, magnesium, and copper were chosen for investigation in the present work, as the dominant loss in each element had been identified as arising from plasma excitation by Nozières and Pines (1958, 1959) and had been correlated with the X-ray absorption fine structure by Leder, Mendlowitz, and Marton (1956). Further, the energy losses in aluminium and magnesium had been previously found to be sharp and in good agreement with the free-electron values of $\hbar\omega_p$, while the prominent loss in copper was broad and considerably different from $\hbar\omega_p$. The dominant losses in each element were well separated, occurring at approximately 10, 15, and 20 eV in magnesium, aluminium, and copper respectively, so that any gradual changes in the basic loss would be easily detectable.

Before the alloy experiments were performed, measurements of the loss spectra of each element were made. The results of such measurements have been discussed elsewhere (Powell and Swan 1959*a*, 1959*b*; Powell 1960*b*) and were sufficient in themselves to clearly identify the origin of the losses. Nevertheless, the alloy results to be presented are interesting and also confirm the previous interpretations. Some of the results from aluminium-magnesium alloys have already been described elsewhere (Powell 1960*a*).

The measurements of the loss spectra of aluminium and magnesium show that the loss spectra of each element consist entirely of combinations of two fundamental energy losses, 10.3 and 15.3 eV in aluminium, and 7.1 and 10.6 eV in magnesium. The larger loss in each metal was identified as the plasma loss and the smaller low-lying loss with the lowered plasma loss predicted to occur at $\hbar\omega_p/\sqrt{2}$ by Ritchie (1957). The copper spectrum was found to consist of a 7.2 eV lowered plasma loss, a 19.9 eV plasma loss, a 27.1 eV combination loss, and a loss of 4.4 eV considered to be due possibly to an intraband transition. Further work (Powell and Swan 1960; Powell 1960*b*) has shown that surface

oxidation of the specimens caused a rapid decrease in intensity of the lowered plasma loss and the appearance of a modified low-lying loss of 7.1 eV in aluminium, 4.9 eV in magnesium, and 3.7 eV in copper.

II. EXPERIMENTAL PROCEDURE

The characteristic loss spectra of electrons scattered through 90° by the targets were obtained with the 127° electrostatic electron spectrometer and apparatus previously described (Powell, Robins, and Swan 1958 ; Powell 1960a). After the target chamber had been gettered by several evaporations of either aluminium or magnesium, the alloy specimens were prepared by heating a helical tungsten filament on which strips of two elements had been placed. This procedure resulted in the deposition of alloys of unknown composition on the target surface and was adopted after attempts to prepare alloys by flash evaporation had proved unsuccessful. Though alloys of unknown composition were prepared by this technique, investigations of the loss spectra of each element had shown the necessity for unoxidized specimen surfaces. A primary electron energy of 1500 eV was used for all measurements.

III. RESULTS

After the simultaneous evaporation of either aluminium and magnesium or of aluminium and copper, a characteristic loss spectrum could be obtained which showed a prominent (plasma-type) loss and a low-lying loss. Typical loss spectra for the elements and the two types of alloys are shown in Figure 1. It was found that in no case could the observed spectra be regarded as arising from the superposition of the spectra of the corresponding pair of elements. It was therefore concluded that alloys had in fact been formed and that there was effectively no separate aggregation of the elements. From the consistency of the results it would also seem that the alloys must have been reasonably homogeneous.

The prominent loss in aluminium-magnesium alloys was observed to occur between 10.6 and 15.3 eV, the values of the plasma loss in magnesium and aluminium. Similarly, the prominent loss in aluminium-copper alloys occurred between 15.3 and 19.9 eV, the observed plasma losses in aluminium and copper. It was found that the low-lying loss changed its position concurrently with the prominent loss ; whereas the low-lying loss increased as the plasma-type loss increased in aluminium-magnesium alloys, it decreased in aluminium-copper alloys as the plasma-type loss increased. The continuous changes in the dominant loss and the low-lying loss between the positions observed in the elements confirm the previous identifications as plasma loss and lowered plasma loss respectively. The variations in the lowered plasma loss are plotted in Figure 2 (b) as a function of the observed plasma energy loss.

As the alloy specimens oxidized, the lowered plasma loss decreased in intensity and was replaced by a modified low-lying loss, as in the elements. The observed modified low-lying loss is plotted against the corresponding plasma loss in Figure 2 (a) ; it is also seen to increase with the plasma loss in the aluminium-magnesium alloys and to decrease in the aluminium-copper alloys.

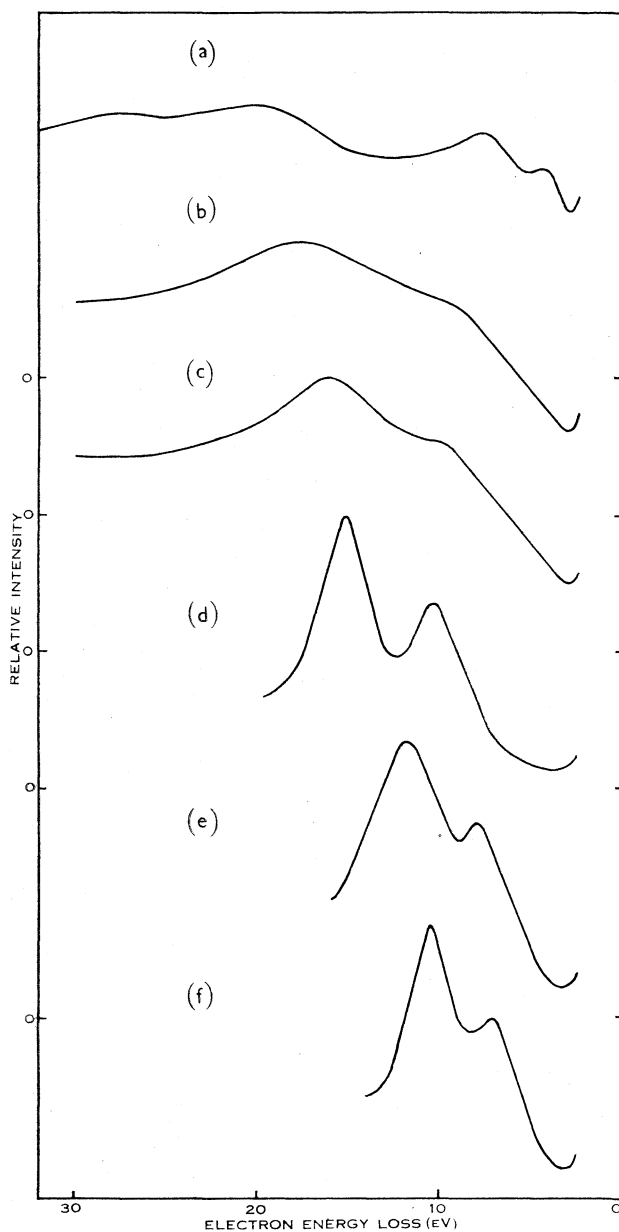


Fig. 1.—Representative portions of characteristic loss spectra of aluminium-magnesium and aluminium-copper alloys together with the loss spectra of the three elements, recorded with a primary electron energy of 1500 eV. Curve (a) is the spectrum of copper, curves (b) and (c) are spectra of aluminium-copper alloys, curve (d) is the spectrum of aluminium, curve (e) is a spectrum of an aluminium-magnesium alloy, and curve (f) is the spectrum of magnesium. The spectra have been drawn so that the plasma peak has the same intensity in all cases.

It was found that the width of the plasma loss peak at half maximum intensity varied considerably in the alloys and the measured half-width is plotted against plasma energy loss in Figure 3 (b). As the half-width of the peak of elastically scattered electrons was 1.9, eV, the true breadth of the plasma peak increased by a maximum factor of approximately 2.5 in the aluminium-

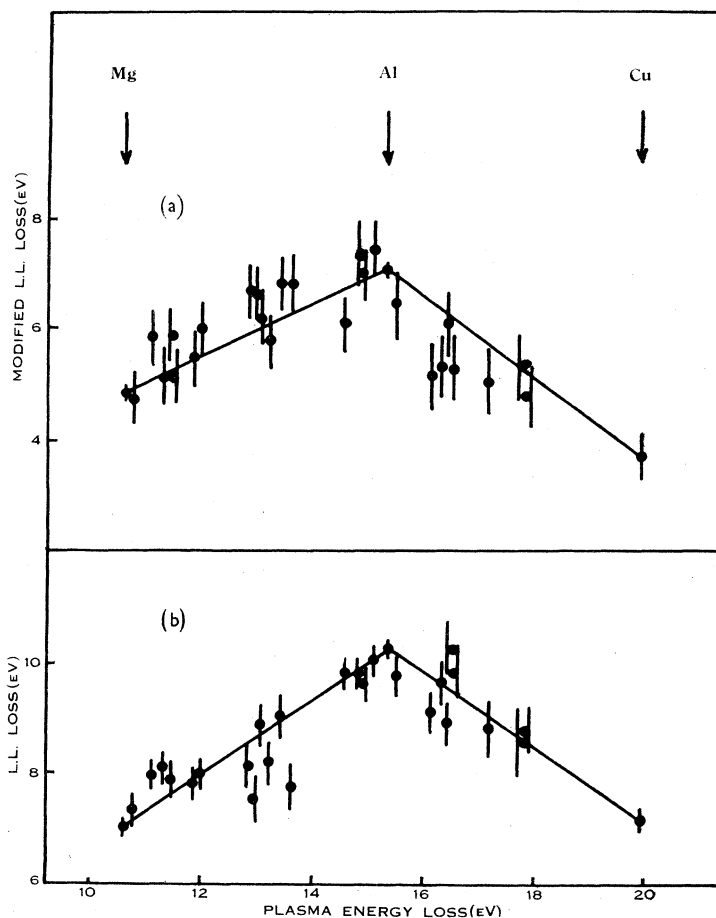


Fig. 2.—The observed modified low-lying loss (a) and the low-lying loss (b) plotted as a function of the corresponding plasma energy loss for aluminium-magnesium and aluminium-copper alloys. Straight lines have been drawn between the points corresponding to the energy losses observed in the elements and are not intended to imply a fit of the alloy data. The probable error in the abscissa is ± 0.2 eV.

magnesium alloys and by a maximum factor of about 9 in the aluminium-copper alloys. In contrast, there is only a gradual increase in the half-width of the lowered plasma loss, as shown in Figure 3 (a). It should be noted that the large errors in the half-widths of the aluminium-copper alloy loss peaks, due to the difficulty in locating the continuous background of inelastically scattered electrons, preclude a more accurate measurement of the half-width variations.

IV. DISCUSSION

It has been found that the loss spectra of aluminium-magnesium and aluminium-copper alloys do not simply arise as combinations of the spectra of the constituent elements. This observation is similar to that of Gauthé (1959), who has recently investigated the loss spectra of several intermetallic compounds.

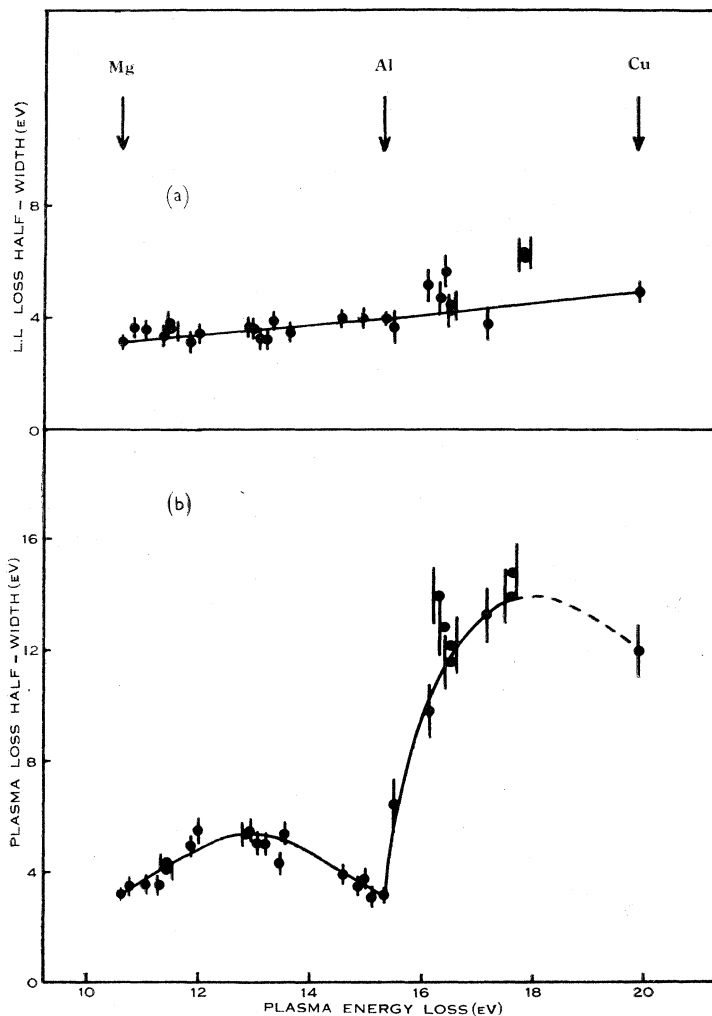


Fig. 3.—The width at half-maximum intensity of the low-lying loss (a) and the plasma loss (b) as a function of the plasma energy loss. Straight lines have been drawn through the points corresponding to the values observed for the elements in (a) and are not intended to represent a fit of the alloy data.

Further, the alloy spectra show a plasma and a lowered plasma loss which both vary continuously between the values observed in the elements. These gradual changes in the energy losses, presumably with composition, confirm the previous collective interpretation of the origin of the losses.

It was suggested in a previous paper (Powell 1960*b*) that the lowered plasma loss could indicate the effective free-electron density in the specimens. This view appears to be confirmed by the observed decrease in the lowered plasma loss with increasing plasma loss in the aluminium-copper alloys. As stated in the introduction, the position of the plasma loss may be determined by considerations other than the free-electron density. Where the plasma loss is displaced from the value estimated using the free-electron density, a large increase in breadth of the loss peak is to be expected. The plasma loss peak in aluminium-copper alloys is thus observed to increase from that found in aluminium, even though the lowered plasma loss and the calculated free-electron density are decreasing. The large increase in breadth of the plasma loss peak is therefore consistent with this interpretation. It is also possible that part of the observed increase in breadth is due to the fact that the conduction electrons are not moving in a uniform lattice in the alloys; variations in the interaction between these electrons and the two types of ions could cause a broadening of the loss peak.

V. CONCLUSION

Measurements of the characteristic loss spectra of aluminium-magnesium and aluminium-copper alloys have shown continuous changes in the positions of the plasma and lowered plasma energy losses found in the elements. Though the alloy compositions were unknown, these variations in the energy losses confirm the previous identifications. It would be of some interest in any future investigation to endeavour to find the relation between loss position and alloy composition.

The present results also show that an investigation of the characteristic loss spectra of alloys can indicate the origin of the energy losses. Though the energy losses in aluminium, magnesium, and copper had been previously identified, the alloy measurements differentiated between the individual particle and collective nature of the origin of the losses. If the loss spectrum of a particular element was so complicated that the origin of the losses could not be otherwise determined, it could be useful to alloy that element with another element whose spectrum was known in order to distinguish between the losses of different origin.

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VII. REFERENCES

- CAUCHOIS, Y. (1952).—*Acta Cryst.* **5**: 351.
- GAUTHÉ, B. (1959).—*Phys. Rev.* **114**: 1265.
- LEDER, L. B., MENDLOWITZ, H., and MARTON, L. (1956).—*Phys. Rev.* **101**: 1460.
- NOZIÈRES, P., and PINES, D. (1958).—*Phys. Rev.* **109**: 1062.
- NOZIÈRES, P., and PINES, D. (1959).—*Phys. Rev.* **113**: 1254.
- PINES, D. (1956).—*Rev. Mod. Phys.* **28**: 184.

- POWELL, C. J. (1960a).—*J. Plasma Physics, Accelerators, Thermonuclear Research* (In press.)
- POWELL, C. J. (1960b).—*Proc. Phys. Soc.* (In press.)
- POWELL, C. J., ROBINS, J. L., and SWAN, J. B. (1958).—*Phys. Rev.* **110**: 657.
- POWELL, C. J., and SWAN, J. B. (1959a).—*Phys. Rev.* **115**: 869.
- POWELL, C. J., and SWAN, J. B. (1959b).—*Phys. Rev.* **116**: 81.
- POWELL, C. J., and SWAN, J. B. (1960).—*Phys. Rev.* (In press.)
- RITCHIE, R. H. (1957).—*Phys. Rev.* **106**: 874.
- RUDBERG, E. (1936).—*Phys. Rev.* **50**: 138.
- RUDBERG, E., and SLATER, J. C. (1936).—*Phys. Rev.* **50**: 150.
- VIATSKIN, A. Ia. (1958).—*Soviet Physics, Technical Physics* **3**: 2252.
- WATANABE, H. (1954).—*J. Phys. Soc. Japan* **9**: 920.
- WATANABE, H. (1956).—*J. Phys. Soc. Japan* **11**: 112.