THE CHARACTERISTIC LOSS SPECTRA OF THE SECOND AND THIRD SERIES TRANSITION METALS*

By M. J. LYNCH† and J. B. SWAN†

[*Manuscript received June* 4, 1968]

Summary

Characteristic electron energy loss spectra are presented for the second and third series transition metals Y, Zr, Nb, Mo, Rh, Pd, Ag, and Hf, Ta, W, Re, Ir, Pt, Au. An identification of most of the spectral features in terms of collective and individual particle excitations is made.

INTRODUCTION

The simple theory of plasmon oscillations in solids (Bohm and Pines 1953) considers collective longitudinal oscillation of the nearly-free electrons and assumes a sharp distinction between these electrons and those tightly bound in the atomic core. This theory has had considerable success when applied to experimental observations of the characteristic electron energy loss spectra of numerous elements; a sharp peak in the spectrum is observed at an energy loss closely corresponding to the plasmon excitation energy. In many other cases, however, modification of the theory is required in order to obtain satisfactory agreement with experiment. This modification may be in the form of a correction in which the polarizability of the inner electrons is allowed for because their binding energy is not large relative to the plasmon energy, or it may take into account the shift in plasmon energy occasioned by single-particle excitations at nearby energies (Nozières and Pines 1958, 1959).

The situation arises for the transition metals in particular, in which there is no obvious distinct separation between the two groups of electrons, the nearly free and the tightly bound. Earlier experiments on the characteristic loss spectra of the first group of transition metals (Robins and Swan 1960) indicated that for elements occurring early in the group the electrons in both the s and d bands must be considered to be free, but that for the elements of higher atomic number some electrons at least in these bands are more tightly bound, as shown by a decrease in plasmon energy below the value given by the simple theory. While such a decrease is predicted theoretically (Nozières and Pines 1958, 1959), no support was found for the prediction that in the first few elements the energy loss would be greater than the value calculated on the assumption that all s and d electrons are essentially free.

It was considered that similar studies of the second and third group of transition metals would be of interest, and accordingly measurements of the characteristic loss spectra of Y, Zr, Nb, Mo, Rh, Pd, Ag, and Hf, Ta, W, Re, Ir, Pt, Au have been made.

* This work was supported by the U.S. Army Research Office and the University of Western Australia.

† Physics Department, University of Western Australia, Nedlands, W.A. 6009.

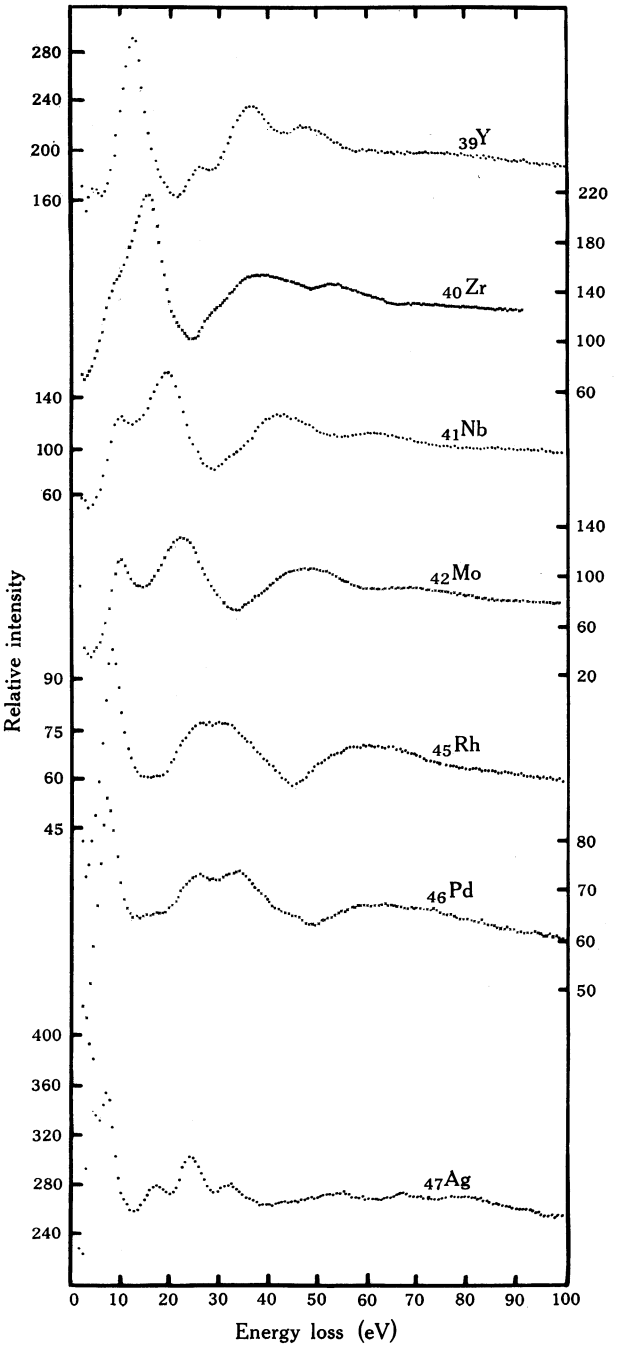

Fig. 1(*a*).—Typical spectra of elements of the second transition group.

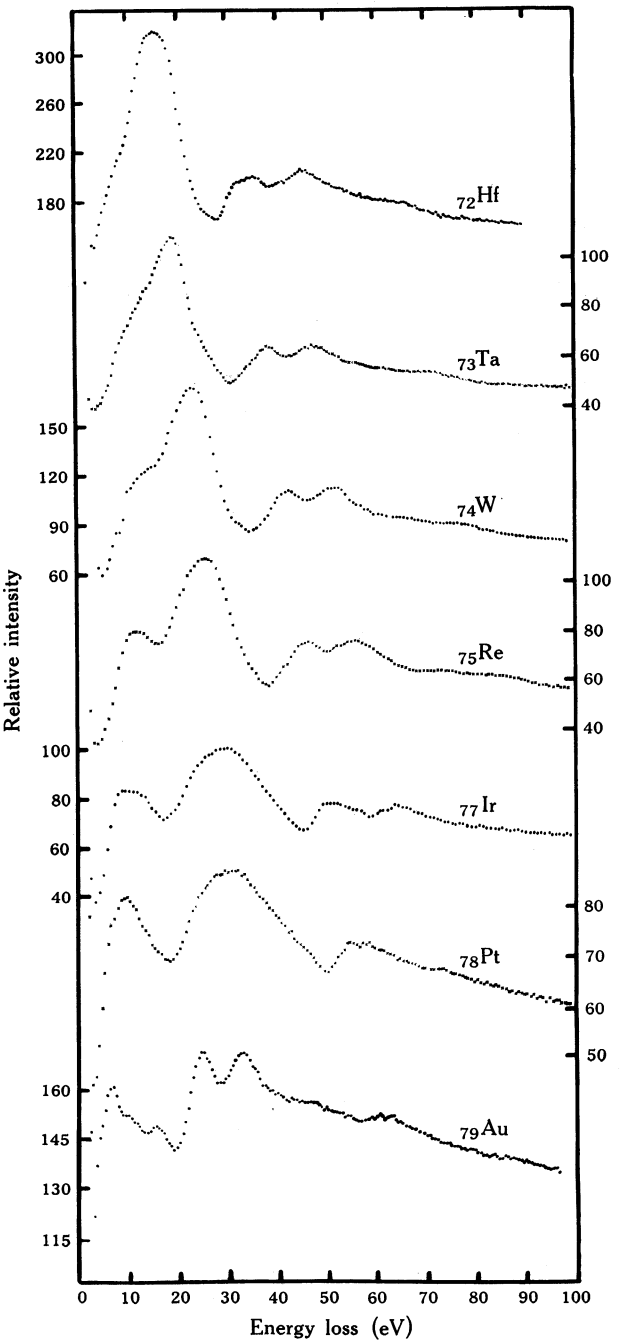

Fig. 1(*b*).—Typical spectra of elements of the third transition group

Apparatus and Procedure

The apparatus used in this work (Swan 1964) and the method of data processing (Hartley and Swan 1966) have been described previously. Briefly, the energy spectrum of a beam of monoenergetic electrons after scattering through 90° in the target material is obtained and stored in a multichannel analyser, and these data are processed by a computer to yield the energy loss value of each peak in the spectrum to an accuracy of $\pm 0 \cdot 1$ eV.

The target was composed of the material under investigation, and a clean surface was maintained either by continuous evaporation (in suitable cases), by scraping, or by having the target as a thin wire and heating it electrically (Hagstrum and D'Amico 1960). Numerous runs were made with each element, operating over a range of primary electron energies and a range of recorded loss energies, to ensure that all observable peaks corresponding to losses of up to 100 eV were measured. The resolution of neighbouring peaks depended on the peak widths and relative intensities and was limited in the apparatus by the primary energy spread of approximately 0·5 eV.

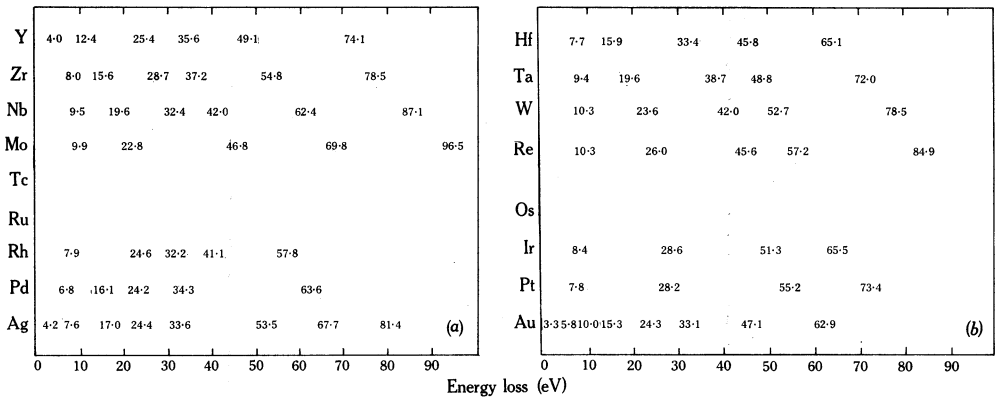

Fig. 2.—Numerical values of the characteristic energy losses observed in elements of (*a*) the second transition group and (*b*) the third transition group. Groupings and trends in values are apparent and comparisons in appearances of the peaks may be made with the aid of Figures 1(*a*) and 1(*b*).

Results and Discussion

Typical spectra observed for the second group of transition metals Y–Ag are shown in Figure 1(*a*), and for the third group Hf–Au in Figure 1(*b*). Remarkable similarities are immediately obvious, as are the trends in shape and energy on progressing through each series. The energy trends are even more clearly illustrated in the scale diagrams of the energy losses given in Figures 2(*a*) and 2(*b*).

Reference to the second transition series shows that the measured energy losses of 12·4, 15·6, 19·6, and 22·8 eV in Y, Zr, Nb, and Mo respectively compare favourably with the theoretical values, $\hbar\omega_p$ (where $\omega_p^2 = 4\pi ne^2/m$, e being the

electronic charge, m the electronic mass, and n the calculated free electron density of the metal assuming all outer s and d electrons are free), of 12·5, 15·3, 19·4, and 23·0 eV, assuming 3, 4, 5, and 6 free s and d electrons respectively.

For the third series of transition metals the loss peaks at 15·9, 19·6, 23·6, and 26·0 eV in Hf, Ta, W, and Re are in good agreement with the theoretical $\hbar\omega_p$ values of 15·7, 19·5, 22·9, and 25·7 eV, assuming 4, 5, 6, and 7 free s and d electrons respectively.

Thus identification of the plasmon loss is obvious for the first four elements of each group, for which the volume loss peak is relatively sharp and intense and occurs at an energy in excellent agreement with the theoretical value. Recent electron energy loss studies (Creuzburg 1966; Daniels 1967) correlated with optical studies indicate that the energy loss peaks observed at 4·2 and 3·3 eV in the Ag and Au spectra respectively are the unresolved surface and volume plasmon losses. The plasmon losses in the remaining two elements of each series are identified, on the basis of appearance and the trends in energy throughout the series, as the 24·6, 24·2, 28·6, and 28·2 eV losses in Rh, Pd, Ir, and Pt respectively. The loss energies in these elements, however, lie below the theoretical values of 30·1, 30·6, 29·5, and 30·2 eV, assuming all s and d electrons effectively free.

Other loss peaks can be identified by appearance and energy also. In particular, the peaks at 49·1, 54·8, 62·4, and 69·8 eV in Y, Zr, Nb, and Mo are in reasonable agreement with the N_1 ionization energies of these elements, while $N_{2,3}$-level ionization in Y, Zr, Nb, Mo, Rh, Pd, and Ag is probably responsible for the losses of 25·4, 28·7, 32·4, 46·8, 57·8, 63·6, and 67·7 eV. The peaks at 65·1, 72·0, 78·5, and 84·9 eV in Hf, Ta, W, and Re are almost certainly due to O_1-level ionization and those at 33·4, 38·7, 42·0, 45·6, 51·3, 55·2, and 62·9 eV in Hf, Ta, W, Re, Ir, Pt, and Au are probably O_3-level ionization. The above interpretation of loss peaks in terms of ionization processes has been supported by measurements made to the point of inflexion of the ionization loss edge rather than to the intensity maxima (Lynch and Swan 1967). The low intensity peaks at 74·1, 78·5, 87·1, and 96·5 eV in Y, Zr, Nb, and Mo resemble ionization peaks, and are possibly also due to ionization processes.

A peak belonging to a distinct set, and being the smallest observed discrete energy loss, is observed in each element except in the Ag and Au spectra where it has not been resolved from the volume plasmon loss. These peaks are interpreted as arising from the surface plasmon excitation. While they do not bear the simple energy ratio to the volume plasmon of $1/\sqrt{2}$, this does not of itself negate the interpretation. The peaks are quite narrow and symmetrical in those elements where they appear with intensities sufficient to enable estimates of widths to be made, and this indicates that they are not due to ionization processes. Their change in relative intensity with changing energy of the primary electrons, together with their sensitive intensity dependence on surface cleanliness, supports the interpretation. The trend of increasing intensity on progressing through the members of each group of transition metals is very similar to the behaviour observed in the first transition group (Robins and Swan 1960).

In several of the elements a relatively intense peak is observed. The energies of these peaks cannot be identified with known ionization processes; however, the similarities in appearance and trends in energy from element to element suggest a common origin. Peaks of this kind, termed "G" peaks, have been described previously (Robins and Swan 1960; Best 1962), and in the present work have energies of 35·6 (Y), 37·2 (Zr), 42·0 (Nb), 45·8 (Hf), 48·8 (Ta), 52·7 (W), 57·2 (Re), 65·5 (Ir), and 73·4 eV (Pt). A hypothesis concerning the origin of these G peaks has been published (Robins and Best 1962), though an alternative interpretation has been recently advanced by Hartley (1968).

Conclusions

From this study of the energy loss spectra of seven elements in each of the second and third groups of transition metals, one peak in the spectrum of each element has been identified with confidence as arising from volume plasmon excitation and another peak has been ascribed to surface plasmon excitation. On the basis of reasonable energy agreement and appearance, other peaks have been associated with ionization occurring in identifiable atomic subshells. A set of broad intense peaks in each group of transition metals has been assigned a common but unidentified origin. In addition several peaks, in the spectra of Ag and Au in particular, have not been considered here in any detail but presumably arise from interband transitions of some kind.

References

Best, P. E. (1962).—*Proc. phys. Soc.* **79**, 133.
Bohm, D., and Pines, D. (1953).—*Phys. Rev.* **92**, 609.
Creuzburg, M. (1966).—*Z. Phys.* **196**, 433.
Daniels, J. (1967).—*Z. Phys.* **203**, 235.
Hagstrum, H. D., and D'Amico, C. (1960).—*J. appl. Phys.* **31**, 715.
Hartley, B. M. (1968).—Ph.D. Thesis, University of Western Australia.
Hartley, B. M., and Swan, J. B. (1966).—*Phys. Rev.* **144**, 295.
Lynch, M. J., and Swan, J. B. (1967).—*Aust. J. Phys.* **20**, 345.
Nozières, P., and Pines, D. (1958).—*Phys. Rev.* **109**, 1062.
Nozières, P., and Pines, D. (1959).—*Phys. Rev.* **113**, 1254.
Robins, J. L., and Best, P. E. (1962).—*Proc. phys. Soc.* **79**, 110.
Robins, J. L., and Swan, J. B. (1960).—*Proc. phys. Soc.* **76**, 857.
Swan, J. B. (1964).—*Phys. Rev.* **135**, A1467.