ELECTRON BINDING ENERGIES IN TRANSITION METALS*†

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It has been suggested (Fahlman *et al.* 1965) that electron binding energies measured by X-ray methods may in some cases be in error by as much as 50%. The electron spectroscopic method (e.g. Hagström 1964; Siegbahn 1965) is claimed to be capable of yielding more accurate values of electron binding energies, and many measurements have been made using this technique, though the majority have been of the binding energies in the inner electronic shells.

Characteristic electron energy loss investigations also provide a means of direct measurement of the electron binding energies, and several measurements of the energy losses suffered by electrons that have initiated ionization processes have been reported (Robins and Swan 1960; Robins and Best 1962). The magnitude of each of these energy losses was determined as the energy separation between the peak resulting from elastically scattered electrons and the peak resulting from electrons that have suffered an inelastic collision in an atomic ionization process.

In X-ray absorption spectra it is generally accepted that relating the energy difference between a bound state and the Fermi energy to the first point of inflection on the absorption curve is based on certain assumptions, which may not always be satisfied; however, this remains at present the most reasonable criterion (Richtmeyer, Barnes, and Ramberg 1934; Parratt 1959).

Energy losses in electron energy loss spectra are conventionally measured to intensity maxima. A better measure of the electron binding energy should result when the difference between the no-loss peak and the point of inflection of the ionization-loss edge is taken; this, in addition, would yield a more satisfactory basis of comparison with X-ray data. The observed width of these "edges" is commonly such that the point of inflection differs from the peak of intensity by several electron volts.

The characteristic electron energy loss spectra of several metals in and near the second and third transition series have been observed and measured recently by the authors. Some of the energy losses have been identified as arising from ionization processes, on the basis of line shape, absolute energy, and change in energy from element to element throughout each series. For these energy losses the results of measurements from the no-loss peak to the points of inflection are presented in Tables 1 and 2, together with an identification of the shell in which ionization is assumed to occur. Included in the tables for comparison with these binding energies are those determined from X-ray investigations (Siegbahn 1965) and it may be observed that there is reasonable agreement between the two sets of results. At these energies this is to be expected for the metals under consideration, as the single-particle transitions predominate over negligible collective electron effects.

The characteristic energy loss method of measuring electron binding energies is comparable in absolute accuracy with an electron spectroscopic method, and has the inherent advantage that the surface condition of the specimen is monitored continuously during observation of the energy loss spectrum.

TABLE 1

A COMPARISON OF BINDING ENERGIES (eV) FOR THE SECOND TRANSITION SERIES METALS

Element	N_1 Ionization		N_2, N_3 Ionization	
	Characteristic Electron Energy Loss Method	X-ray Values	Characteristic Electron Energy Loss Method	X-ray Values
Y	45·2	47	23·6	25
Zr	52·0	52	27·7	29
Nb	57·8	58	31·2	34
Mo	64·5	63	37·9	34
Rh			48·5	47
Pd			52·0	51
Ag			63·9	58–65

TABLE 2

A COMPARISON OF BINDING ENERGIES (eV) FOR THE THIRD TRANSITION SERIES METALS

Element	O_1 Ionization		O_3 Ionization	
	Characteristic Electron Energy Loss Method	X-ray Values	Characteristic Electron Energy Loss Method	X-ray Values
Hf	61·7	65	30·3	30
Ta	69·1	71	34·8	34
W	74·7	75	38·4	36
Re	81·1	87	41·9	40
Ir			48·8	52
Pt			51·7	52
Au			58·7	59

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