

INVESTIGATION OF 4-*d* TRANSITION METALS (Y, Zr, Nb, Mo) USING THE METHOD OF SOLID STATE PLASMA

BY H. B. KOŁODZIEJ, J. OLESIK AND U. MADALKIEWICZ

Department of General Physics, Pedagogical University of Częstochowa*

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The method of discrete energy losses of electrons scattered on the surfaces of flat samples of Y, Zr, Nb and Mo was applied to measure the energy of plasmon excitations. The electron energy losses were measured on polycrystalline high purity samples in vacuum of the order 10^{-7} hPa. Measurements were made with a "Riber" quadrirreticular analyser with an electric retarding field. The obtained spectra of characteristic energy losses allow one to expect the existence, in the group of transition *d*-metals Y, Zr, Nb and Mo, of two components of volume plasmons corresponding to the excitation of *s* and *d* electrons.

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1. Introduction

Investigation of characteristic energy losses of electrons (EELS) scattered on the surfaces of 3-*d* transition metals established that there occurs an excitation of "condensed" volume plasmon in a hybridized collective of *s*+*d* electrons in the metals, and independently from the above, "band" volume plasmons of both subsystems of electrons *s* and *d* become excited [1], [2].

The EELS measurements of electrons scattered on the surfaces of Y, Zr, Nb and Mo, carried out in our laboratory were aimed at testing whether the point of view is correct also for other groups of transition metals.

According to Feynman [3] and Pines [4], use of the classical approximation of the free electron gas allows one to show that the frequency of plasmon excitation is expressed by the formula:

$$\omega_p^2 = \frac{4\pi n_0 e^2}{m}, \quad (1)$$

where n_0 is the concentration of electrons or holes; e , m — respectively, charge and mass of an electron. Then, it is easy to proceed to the formula for volume plasmon excitation

* Address: Wyższa Szkoła Pedagogiczna, Zawadzkiego 13/15, 42-200 Częstochowa, Poland.

energy:

$$\Delta E_v = \hbar\omega_p. \quad (2)$$

Metals of complex electron structure such as transition *d*-metals have a very complicated energy spectra [1], [2], and [5].

Interpretation of the spectra becomes complex in view of the difficulties, in interpretation of the complex collective character of conduction *s-d* electrons and determination of the compact electron band in atomic cores.

An attempt to interpret the complex spectra of energy losses for certain 4*d*-transition metals, Y, Zr, Nb and Mo, is made in this paper.

2. Experimental set-up

The EELS were measured with the type OPR-304 "Riber" quadrirreticular analyser with an electric retarding field. A block diagram of the power supply and detection system which were constructed in our laboratory, is shown in Fig. 1. The measured energy resolving power of the whole measurement system does not exceed 0.5 eV. Incident electrons' energy was 150 eV.

3. Results and discussion

The investigation was carried out on polycrystalline samples of 99.99% purity. The surfaces were polished mechanically and cleaned by means of a "bombarding" electron beam in the analyser. For certain samples cleaning lasted up to several hours, until the current of each sample was stabilized. The EELS obtained for Y, Zr, Nb and Mo are shown in Fig. 2.

Numerical values for losses, corresponding to particular peaks, which were determined in relation to the highest peak (peak without losses) were read from the energy spectra. The values of energy losses for the investigated metals obtained from this are listed in Table I.

Low energy losses whose explanation is possible only under ultrahigh vacuum conditions, when the impurities have been radically eliminated from the surfaces of the investigated samples, are listed in column ΔE_0 .

Detailed analysis of the data obtained for Y, Zr, Nb and Mo gives rise to a conclusion that the energy losses ΔE_1 and ΔE_2 are responsible for the excitations of the two components of the volume plasmon, respectively: the component *s* and the component *d*, whereas the energy of the whole volume plasmon is determined by the energy loss ΔE_3 .

The losses which are a linear combination or multiple of basic losses ΔE_i are listed in column A_i .

Number *n* of electrons per atom equivalent to the value of the energy loss ΔE giving rise to the excitation of the volume plasmon can be easily determined in the free electron approximation from formula (2):

$$n = \frac{(\Delta E)^2 A}{B^2 e}; \quad B = \hbar e \left(\frac{4\pi N_A e}{m} \right)^{1/2}, \quad (3)$$

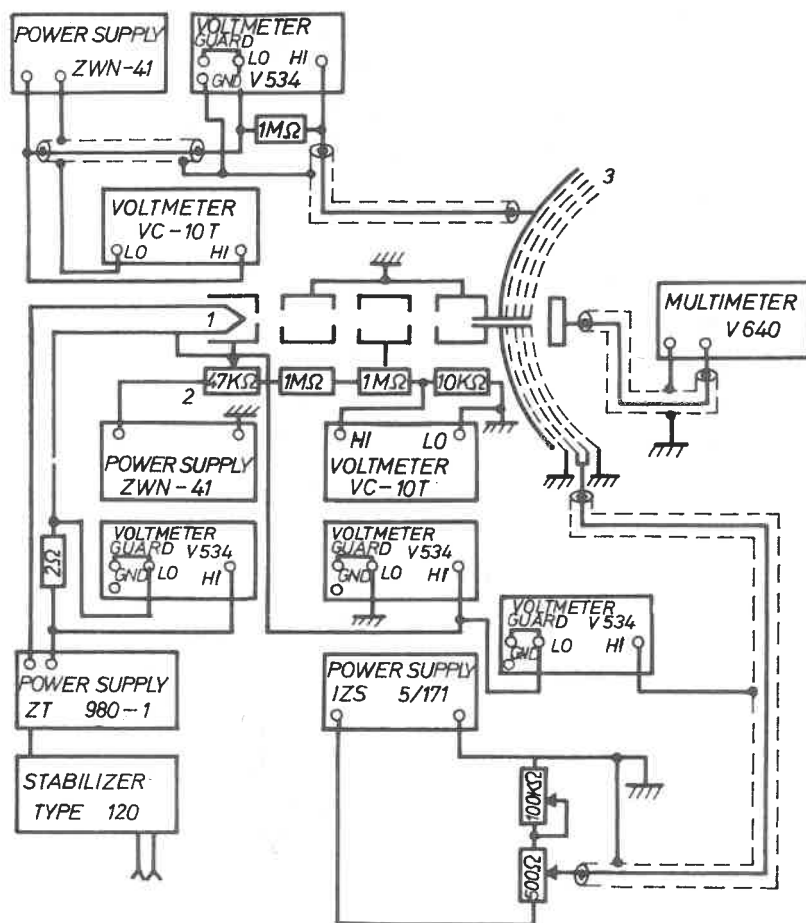


Fig. 1. Block diagram of the power supply and detection systems: 1 — electron gun, 2 — voltage divider, 3 — analyzer OPR-304

TABLE I

List of numerical values of energy losses for Y, Zr, Nb and Mo

Metal	Valence electrons	ΔE_0 [eV]	ΔE_1 [eV]	ΔE_2 [eV]	ΔE_3 [eV]	A_i [eV]
Y	$5s^2 4d^1$	2.0	6.5	9.2	10.8	16.4; 17.9; 19.5; 21.2
Zr	$5s^2 4d^2$	6.3	10.4	11.4	15.2	18.4; 21.7; 23.8; 25.6
Nb	$5s^1 4d^4$	4.3	8.8	17.5	19.7	12.5; 15.3; 22.0; 24.0
Mo	$5s^1 4d^5$	7.8	9.2	20.8	22.8	15.8; 17.2; 23.3; 24.9

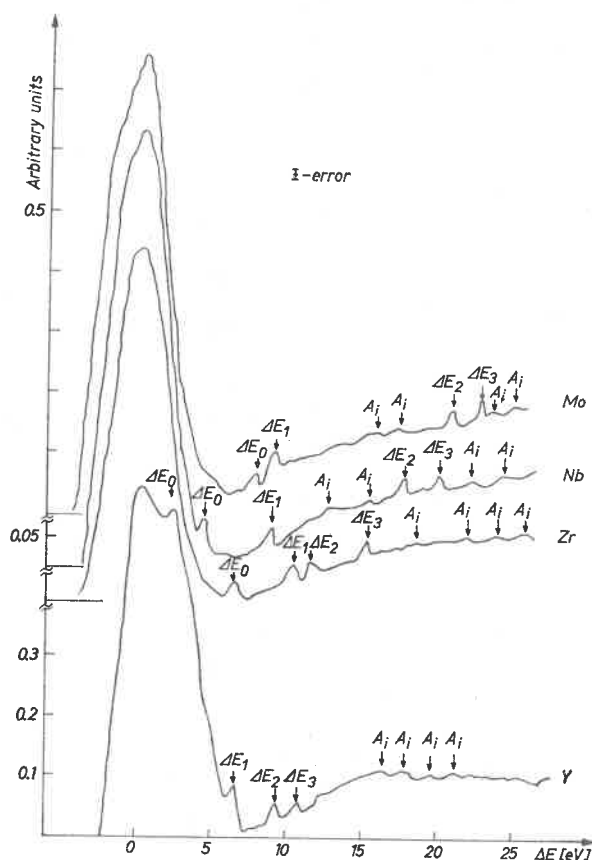


Fig. 2. Spectra of characteristic energy losses for Y, Zr, Nb and Mo

where A is the atomic mass, ρ — density, N_A — Avogadro's number. Numbers n_1 and n_2 are calculated from the losses ΔE_1 and ΔE_2 , and the number of electrons n_3 calculated from the loss ΔE_3 are given in Table II.

Numerical values of n_1 and n_2 are similar to the numbers n_s and n_d of the electrons s and

TABLE II

Numbers of electrons n_j per atom computed from the corresponding energy losses ΔE_j

Metal	Valence electrons n_s, n_d	Subgroup s		Subgroup d		Subgroup $s+d$	
		ΔE_1 [eV]	n_1	ΔE_2 [eV]	n_2	ΔE_3 [eV]	n_3
Y	$5s^2 4d^1$	6.5	1 ± 0.15	9.2	2 ± 0.2	10.8	2.8 ± 0.26
Zr	$5s^2 4d^2$	10.4	1.8 ± 0.18	11.4	2.2 ± 0.2	15.2	3.9 ± 0.26
Nb	$5s^1 4d^4$	8.8	1 ± 0.1	17.5	3.9 ± 0.2	19.7	5.1 ± 0.26
Mo	$5s^1 4d^5$	9.2	0.96 ± 0.1	20.8	4.9 ± 0.24	22.8	5.9 ± 0.26

d in the respective metals. Furthermore, numerical values of n_3 are good approximations corresponding on one hand to their sums $n_1 + n_2$ and on the other to the total number of electrons $s + d$ in the investigated metals, within the margin of error.

4. Final conclusions

Results of the investigation of the excitation of electron plasma oscillations in yttrium, zirconium, niobium and molybdenum suggest that there occurs an excitation of "condensed" volume plasmon in the collective of $s + d$ free electrons in the metals, and, independently, there occurs an excitation of the "band" volume plasmons of both subgroups of s and d electrons. This implies the existence of a certain "individuality" imposed by the electron structure of an isolated atom, which does not cease to exist in the process of collectivization of valence electrons in metals. It confirms the hypotheses brought forward by the authors in [1].

Investigation of electron plasma of other transition metals carried out in our laboratory will allow us to test whether the hypothesis is correct and universal in relation to all transition metals.

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