High-intensity transition in the low-energy part of the electron-energy-loss spectra of Yb and related metals

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The origin of a high-intensity transition positioned in the low-energy region of the electron-energy-loss spectra of Yb and related metals is discussed. Considering the systematics in the $4f$ series, the behavior of the real part of the dielectric function, band calculations, gas-phase data, and the variation in the intensity of the energy loss as a function of primary electron-beam energy, we deduce that the strong excitation originates from an interband transition involving single-particle excitations of valence electrons.

INTRODUCTION

Information on low-energy electronic excitations in the rare-earth-metal group is available from high-energy electron-transmission experiments,[1,2] optical reflection and absorption data,[3,4] and reflection electron-energy-loss measurements.[5–10] In the last category of experiments, Netzer, Strasser, Rosina, and Matthew[6] recently presented a comprehensive study of the lanthanide series. There is general agreement in the literature on the characterization of the excitation in the low-energy loss regime, 5—30 eV, in terms of collective excitations, band transitions, and single particle excitations. A better mapping of the electronic excitations close to the elastic peak (the energy interval 0.5—10 eV) was obtained during the last years in reflection electron-energy-loss spectroscopy (REELS) due to the improved energy resolution compared to that obtainable in the transmission mode. It should also be emphasized that the dipole selection rules governing the optical excitations are not fulfilled in the electronically excited transitions for primary electron-beam energies below 1 keV.

In this Brief Report we discuss the origin of a strong low-energy excitation observed in the electron energy-loss spectra, at 3—5 eV, of certain elements in the lanthanide group. This is the most intensive feature in the energy-loss spectra of Eu and Yb for primary beam energies in the interval of 100—2000 eV. Another characteristic feature of these excitations is the extraordinarily small value of the FWHM. Besides the comparison of electron energy loss spectra of the $4f$ elements themselves, it is useful to draw an analogy to the low-energy region of similar electron excitation spectra of the alkaline earths, which have electronic configurations bearing much resemblance to those of Eu and Yb. Also, the electron energy loss spectrum of Yb in the gas phase,[11] the only one available of the rare-earth metals, provides information on the pronounced excitation. The electron-energy-loss spectrum of silver exhibits a strong peak in the low-energy region. Much information is available on this peak, both in terms of optical data[3] in the considered energy region, and in terms of high-energy electron-transmission results,[12,13] and data from REELS measurements.[14]

RESULTS AND DISCUSSION

The electron-energy-loss measurements were carried out in an UHV system with a base pressure below 1.3×10^{-8} Pa. Thin films of Yb and Ca were deposited on a stainless-steel backing in a preparation chamber, which is in direct connection with the analyzing chamber via a valve. The evaporation rate was 1 Å/s as measured with a quartz-crystal microbalance. In the case of silver, a high-purity (99.999%) foil was cleaned by a combination of 2-keV argon-ion bombardment and annealing, a process which also took place in the preparation chamber. X-ray-induced photoelectron spectroscopy (XPS), Auger electron spectroscopy, and REELS, were used for characterization of the samples and the electron excitation studies. Because of ytterbium's high affinity to oxygen, the presence of this element was checked before and after the loss measurements. A 150° hemispherical analyzer with a three-lens input system was used for energy analyses of the emitted electrons. A typical energy resolution of 0.44 eV, corresponding to the FWHM of the elastically reflected electrons, was applied for the electron-energy-loss measurements.

Figure 1 shows the energy-loss spectrum of 121- and 297-eV electrons reflected from an Yb film. The energy-loss peak, positioned at 4.3 eV, has a high intensity, and the FWHM is considerably smaller than that of the bulk plasmon positioned at 9.3 eV. These features in the spectrum, and the behavior of the background, are in agreement with the results given in Ref. 6. Also, in Ag (Fig. 2) the low-energy-loss spectrum for a primary electron beam energy of 400 eV, is dominated by an intense and sharp excitation at 3.9 eV. The energy loss at 4.3 eV in Yb and a related loss in Tm, were published earlier.[8,9] Two different primary electron beam energies, 100 eV and 300.8 eV, were used to excite electrons in Ca. As shown in Fig. 3, energy-loss structures occur at 3.6 and 7.5 eV, again, with a very pronounced and narrow low energy peak.

In order to structuralize the discussion of the assignment of the 4.3 and 3.8 eV excitations in Yb and Eu respectively, the following three possibilities are treated: (i) interband transitions involving $4f$ electrons, (ii) collective excitations, and (iii) interband transitions involving

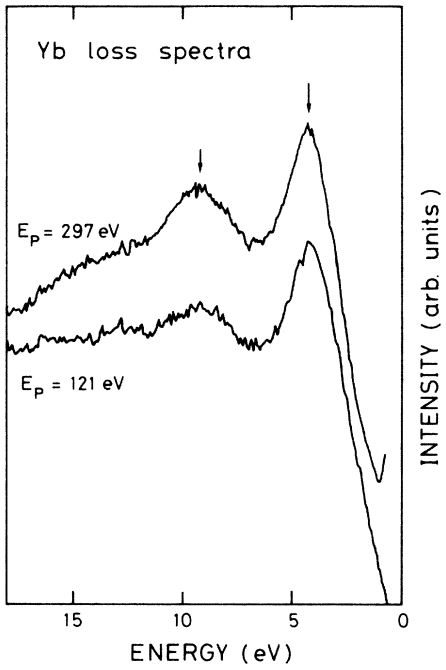

FIG. 1. Reflection electron-energy-loss spectra recorded in $N(E)$ mode from an Yb film. Primary electron beam energies were 121 and 297 eV. The scattering angle was 155°.

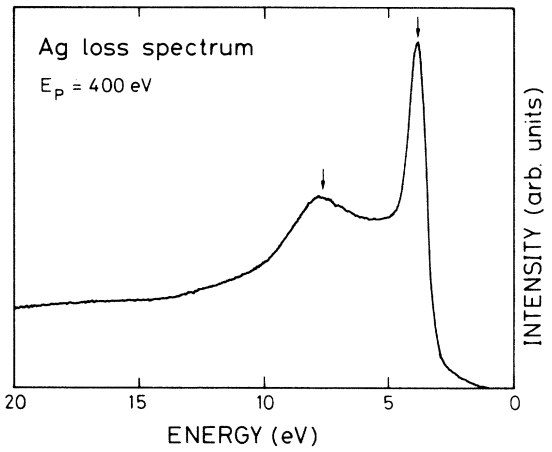

FIG. 2. The energy-loss spectrum from Ag taken with a primary electron beam energy of 400 eV exhibits a sharp excitation at 3.9 eV.

single particle excitations of valence electrons.

(i) Table I contains the electronic structure, the energy position of the maximum in the $4f$ level distribution as measured with XPS, qualitative statements on the intensities of the excitations considered in the lanthanide group and related metals, and the energy positions of the excitations. Eu and Yb are very similar in several respects. Both have a valence state 2, the structures of the bremsstrahlung isochromat spectra[16] have much resemblance, and the top edges of the $4f$ levels lie close to the Fermi level. However, an assignment of the strong transition based on excitations involving $4f$ electrons alone can be ruled out considering the systematics in the series and comparing the positions of the observed energy losses around 4 eV with the binding energies of the $4f$ electrons, $E_B(4f)$. In Sm, Gd, Ho, Er, and Tm, where the excitations are pronounced, $E_B(4f)$ is larger than the loss energy. Besides, the smallness of the atomic cross sections also excludes $4f$ transitions as the explanation of the strong feature in the loss spectra. Furthermore, the role of the f electrons is diminished since the strong excitation is observed in the alkaline earths as demonstrated in Fig. 3. The energy-loss spectra of Ca, Sr, and Ba in the high-energy electron-transmission mode were measured by Langkowsky,[17] who found energy losses in the 3.2—4.3 eV range with small half-widths.

The influence of different selection rules is probably the explanation of the very pronounced 3.9 eV peak in REELS compared to the transmission results.

TABLE I. Binding energies of the $4f$ levels are taken from Refs. 15 and 16. The intensities of the excitation discussed are estimated in a qualitative way mainly from Ref. 6 and the present work. The abbreviation V.S. means very strong, S. means strong, and V.W. means very weak.

Element	Electronic structure	$E_{B_p}(4f)$ (eV)	$I(\sim 4$ eV)	E_{exc}
Ca	$[Ar](4s\,3d)^2$		S.	
Ce	$[Xe]4f^1(5d\,6s)^3$	1.9	V.W.	3.3
Pr	$-4f^2(5d\,6s)^3$	3.5	V.W.	
Nd	$-4f^3(5d\,6s)^3$	4.9	V.W.	3.8
Pm	$-4f^4(5d\,6s)^3$			
Sm	$-4f^5(5d\,6s)^3$	5.0	S.	2.9
Eu	$-4f^7(5d\,6s)^2$	1.9	V.S.	3.8
Gd	$-4f^7(5d\,6s)^3$	7.6	S.	4.6
Tb	$-4f^8(5d\,6s)^3$	2.2	V.W.	5.0
Dy	$-4f^9(5d\,6s)^3$	3.9	V.W.	4.0
Ho	$-4f^{10}(5d\,6s)^3$	5.0	S.	4.0
Er	$-4f^{11}(5d\,6s)^3$	4.8	S.	3.8
Tm	$-4f^{12}(5d\,6s)^3$	4.7	S.	3.9
Yb	$-4f^{14}(5d\,6s)^2$	1.2	V.S.	4.3

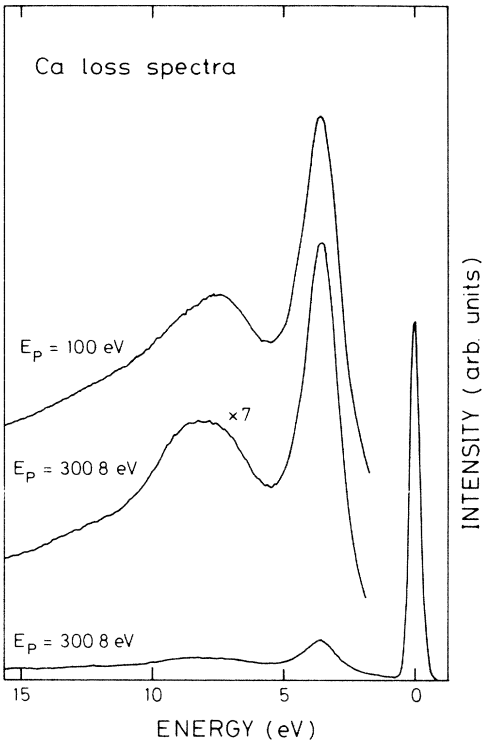

FIG. 3. Electron-energy-loss spectra of Ca for primary beam energies 100 and 300.8 eV. In the last case the elastic peak is included for comparison.

(ii) The bulk plasmon in divalent Yb is observed at 9.3 eV in reasonable agreement with the value predicted in the free electron theory assuming two free electrons per atom. This assignment is confirmed by the width of this excitation, its intensity variation as a function of primary beam energy, and the systematics in the $4f$ series. A further argument is the shift of this peak toward higher loss energies when oxygen adsorption[10] or mixing with another metal takes place.[9] There is still an appreciable intensity in the low-energy-loss peak of Yb when the primary electron beam energy is increased to 1500 eV, which excludes an assignment as a surface plasmon. Valence-band satellites in the $4f$ photoemission spectra of Eu and Yb were discussed by Schneider *et al.*,[18] who interpreted these satellites to be caused by collective conduction electron excitations and not $4f$-$5d$ shake-up induced changes in the $4f$ occupation number. In the case of Ca, synchrotron radiation photoemission studies[19] of the valence band and the region around the $3p$ core level showed intense satellites which were interpreted as plasmon satellites. There is agreement between the photoemission data and the electron-energy-loss results concerning the energetic positions of the two excitations and the assignment of the loss feature at 8 eV as a bulk plasmon. However, the surface plasmon is positioned much nearer to the bulk plasmon than the strong peak at 4 eV. This can be observed in the loss spectra of Ca in Fig. 3, where the centroid of the broad peak shifts towards a lower energy when the beam energy is lowered from 300—100 eV.

The peak observed at 3.9 eV in Ag (Fig. 2) is well known in both optical studies and high-energy electron transmission experiments.[3,13] Optical data show that $\epsilon_1(\omega)$ passes through zero at 3.2 eV instead of 9.2 eV as expected from the $\hbar\omega_b$ value using a free-electron model. The peak is a modified plasmon pushed to lower energy by the onset of the d-band threshold.[20]

A significant point that distinguishes Yb from Ag, concerning the nature of the intense 4-eV peak, is the behavior of $\epsilon_1(\omega)$ in Yb. From optical data[4] $\epsilon_1(\omega)$ passes through zero at 8 eV, near the position of the bulk plasmon determined by electron transmission and reflection measurements. Thus, the excitation mechanisms for the peak at 4 eV in Ag and Yb are different.

(iii) The third possibility is a valence-band excitation involving electrons of s, p, and d characters in the upper part of the valence band. In the vapor phase,[11] the electron-energy-loss spectrum of Yb exhibits a loss peak at 3.2 eV, which is assigned as a $6s^2 \rightarrow 6s\,5d$ transition. An energy shift of 1.2 eV, and a slight broadening of the peak, can be attributed to solid-state effects including screening. A comparison of the intensity of the 4.3 eV excitation to the elastic peak intensity shows no strong energy dependence, which indicates an interband transition. Support for an interpretation in terms of single-particle excitations is found in band-structure calculations of Skriver,[21] and Johansen and MacKintosh.[22] Narrow peaks, mainly of d character, occur above the Fermi level, while the $6s$-density of states below the Fermi level is smeared out. Interband transitions corresponding to the observed peaks can be established.

In summary, the very similar electron-energy-loss spectra of Ca, Eu, and Yb exhibit a bulk plasmon around 8 eV. The intense peaks at 4 eV can be explained as single-particle excitations of valence electrons.

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