EXPERIMENTAL EVIDENCE OF OPTICAL EXCITATION OF 4f ELECTRONS IN Yb

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Uv photoemission measurements on evaporated films of Yb are reported. The results locate the spin-orbit–split 4f states at 1.20 and 2.50 eV below the Fermi level.

Calculations of the band structure of rare-earth metals have not been able to locate accurately the position of the 4f levels, a consequence of the sensitivity of their energies to the exact form of the exchange.[1] It is therefore of particular importance to be able to determine the positions of these levels by experimental means. Several attempts have been made in the past to optically excite the 4f electrons in rare-earth metals without notable success. Recent uv photoemission measurements[2] on Eu indicated slight evidence for transitions from 4f states lying 2 to 3 eV below the Fermi level. In this Letter we wish to report on photoemission measurements using photon energies up to 21.2 eV on evaporated films of Yb which reveal clearly structure due to transitions from 4f states.

All measurements were made on Yb films evaporated from a tungsten basket onto a glass substrate. The energy distribution curves (EDC's) of the photoemitted electrons were obtained as the first differential of the photocurrent by modulating the retarding voltage between the sample and a surrounding collector can. Measurements with photon energies less than 11 eV were made with the specimen chamber coupled to a uv monochromator via a LiF window. The pressure in the chamber, normally 3×10^{-10} Torr, rose to 5×10^{-8} Torr during evaporation. Helium resonance radiation of photon energy 21.2 eV was obtained with a discharge lamp connected directly to the chamber. To reduce the risk of contamination the working pressure was kept below 2×10^{-8} Torr by isolating the sample region from the relatively high pressure in the lamp with two capillaries and by using differential pumping.

EDC's obtained with photon energies up to 10.6 eV are shown in Fig. 1. The results, which have been normalized to the yield, are plotted on a reduced scale $E_{kin}+e\varphi-\hbar\omega$, where E_{kin} is the electron kinetic energy, and $e\varphi$ the work function of the sample. From a Fowler plot of the yield near threshold, $e\varphi$ was deduced to be 2.88 eV. Various features in the spectra are observed which remain at constant position on the reduced scale in agreement with nondirect transitions from features in the initial density of states or direct transitions from states of low dispersion. As the photon energy is increased, two peaks A (−1.2 eV) and B (−2.5 eV) grow in strength (relative to the other structure). For a photon energy of 21.2 eV (Fig. 2) A and B are in fact the only features that can be discerned at the high-energy end of the Yb spectrum. By comparison,

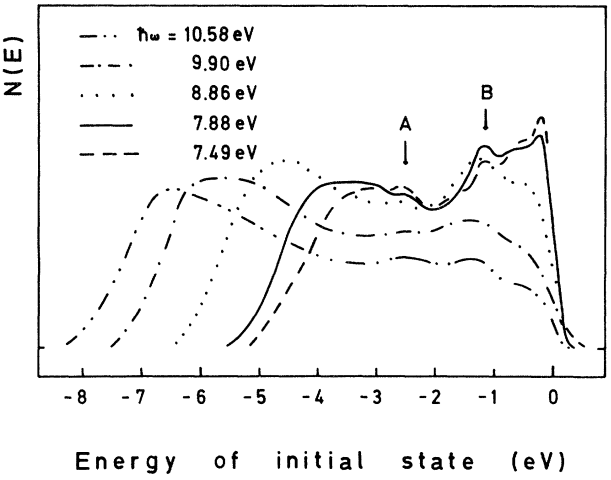

FIG. 1. EDC's obtained from Yb at different photon energies.

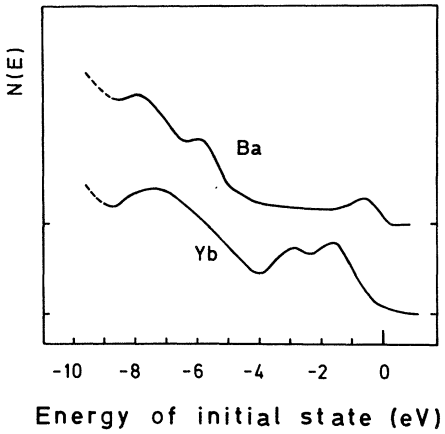

FIG. 2. EDC's obtained from Yb and Ba films for $\hbar\omega = 21.2$ eV. The structure below −5 eV is probably due to contamination.

the result for Ba shows only a single feature immediately below the Fermi level which has been associated with transitions from the partially filled $5d$ band.[2] We therefore interpret the peaks at A and B as the spin-orbit–split $4f$ levels of Yb. The midpoint of the peaks corresponds well with the center of a peak observed with lower resolution in the x-ray photoemission spectrum of evaporated Yb films.[3]

The band structure of Yb metal has recently been calculated by Johansen and Mackintosh using the relativistic augmented plane wave method. In common with other rare-earth metals the outer electronic structure is characterized by a $6sp$ band hybridized with a broad $5d$ band which overlaps the Fermi level. The photoemission structure which extends from the Fermi edge to about -2 eV and which is more apparent in the EDC's obtained with low photon energies is immediately associated with transitions from the occupied $5d$ states. The calculated positions of the $4f$ levels (4.4 and 2.95 eV below the Fermi level) are lower than the positions as deduced from the EDC's. The measured spin-orbit splitting 1.30 ± 0.05 eV compares with Johansen and Mackintosh's value of 1.45 eV and with 1.22 eV as calculated by a modified Hartree-Fock method for a free atom.[4]

The weakness of the $4f$ peaks at low photon energies as compared with the strength of the $5d$ band, which contains less than 2 electrons/atom, is consistent with optical results obtained by Müller and recently by Endriz and Spicer.[5-7] In neither case was there conclusive evidence of excitations of the $4f$ electrons. We note that the positions of two small features at 1.2 and 2.8 eV observed by Endriz and Spicer in the absorption spectrum of Yb but not in that of Sr correspond fairly well with the positions of the $4f$ peaks relative to the Fermi edge in the present EDC's. According to the band structure calculation the $5d$ band extends from below the Fermi level to approximately 6 eV above.

The weakness of the $4f$-$5d$ transition for photon energies less than 8 eV must reflect the corelike nature of the $4f$ orbitals. As they are localized within a closed $5s$, $5p$ shell, overlap with the band states is small compared with the overlap of band states with themselves.

The increased relative strength of the $4f$ features at higher photon energies reflects the increased plane-wave–like nature of the final states. For photon energies above 8 eV, the $4f$ electrons are excited to states of sp character and such excitations are forbidden according to electric dipole selection rules. These excitations are allowed for $5d$ electrons, however. As one increases the photon energy the $4f$ and $5d$ electrons are excited to higher energies in the continuum, where the electrons are more free-electron like. Thus, these final states should contain a larger proportion of components with high l quantum numbers. Transitions from the filled $4f$ states should therefore become more important relative to transitions from the $5d$ states, as one increases the photon energy.

A complete report on uv photoemission measurements of Yb, Eu, and Ba will be presented at a later date.

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