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He II spectra of La, Ce and Yb: Novel features in the valence band region*

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Abstract. He II photoelectron spectra of La, Ce and Yb show features which cannot be explained in terms of single electron excitations. It is proposed that these are due to formation of electron-hole pairs.

Keywords. UPS; valence fluctuation; valence band; rare earth metals.

We have been interested in the investigation of electron states in rare earth materials for some time (Rao and Sarma 1980). During the course of these investigations, we have observed unusual features in the valence bands of La, Ce and Yb which cannot be accounted for by the known electronic configurations of these metals. These features appear as sharp peaks in the valence band region and seem to represent an electronic process occurring in the bulk of the metal and not due to a surface effect. Such structures have been noticed at times (Steiner *et al* 1977; Baer *et al* 1981; Gudat *et al* 1981; Alvarado *et al* 1980), though with poor resolution (Steiner *et al* 1977; Baer *et al* 1981; Gudat *et al* 1981), and attributed to surface states (Gudat *et al* 1981; Alvarado *et al* 1980). We have investigated these features in the valence band region to understand their nature and origin and their possible relevance to the problem of spontaneous valence fluctuation.

In figure 1, we have shown the He II spectra of La, Ce and Yb. Lanthanum with the $4f^0\,(6s,\,5d)^3$ configuration is expected to show a single peak (marked 1 in figure 1) near the E_F originating mainly from 5*d*-states, but we see two additional peaks at 2·1 and 3·5 eV (marked 2 and 3 respectively) in the spectrum. These features of La have not been described hitherto in the literature. Cerium is expected to exhibit a single structure due to 4*f* emission, besides an emission at E_F due to the conduction band (peak 1 in figure 1); we however see two peaks (2 and 3) besides peak 1. Peak 2 which appears distinctly in the spectrum shown in figure 1 has been noticed as a shoulder or an asymmetry on the higher binding energy side of the conduction band in earlier studies (Steiner *et al* 1977; Baer *et al* 1981). Ytterbium shows a weak feature due to the conduction band near E_F in He II spectra; in addition it shows four peaks (marked 1, 2, 3 and 4 in figure 1) due to 4*f*-emission instead of the expected doublet due to the spin-orbit split structure.

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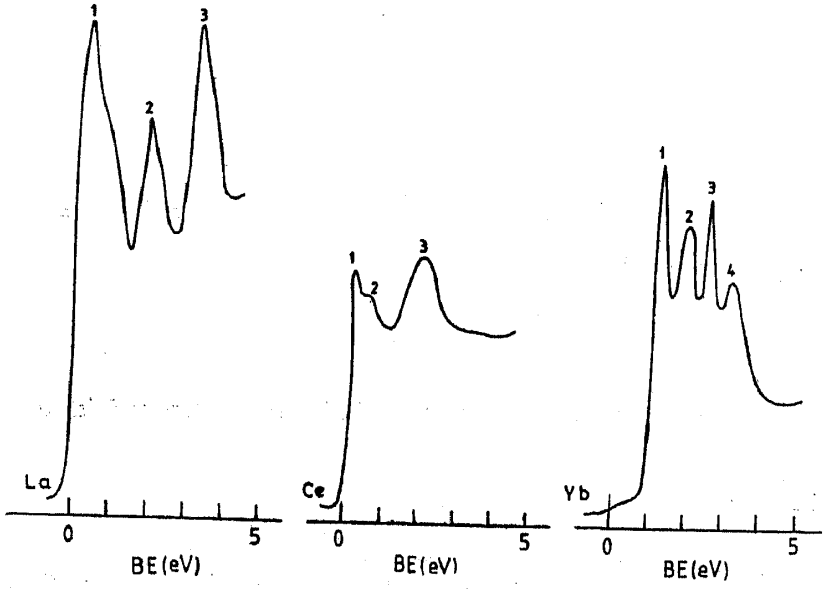

Figure 1. UV photoelectron spectra of La, Ce and Yb using He II radiation; various peaks in the spectra are marked by numbers.

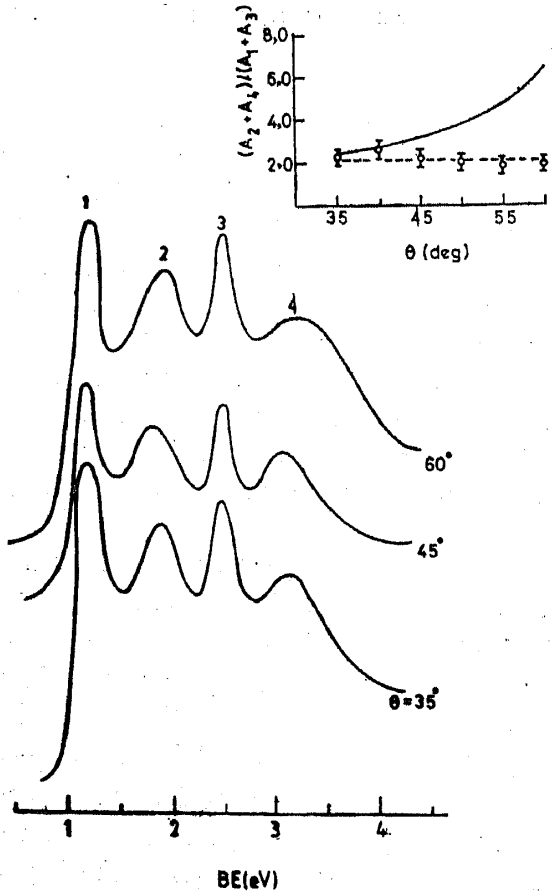

Figure 2. UV photoelectron spectra of Yb using He II radiation at various angles of acceptance into the analyzer. In the inset, the intensity ratio of peaks 2 and 4 to that of peaks 1 and 3 is plotted against the acceptance angle, θ, measured from the normal to the sample surface; the solid curve indicates the expected trend of the ratio if peaks 2 and 4 were due to surface states.

To investigate whether the additional features found in the valence band region could arise from surface states, we recorded the spectra of Yb inclined at various

angles of acceptance, θ (figure 2). We see that the relative intensities of the various peaks remain constant over the entire range of θ. The ratio of the combined areas of peaks 2 and 4 to that of peaks 1 and 3 have been measured by fitting the background subtracted spectra with four gaussians and the result is plotted against θ (figure 2, inset).

Alvarado *et al* (1980) have observed marked changes in the relative intensities of the peaks of Yb with the energy of the radiation and have therefore attributed peaks 2 and 4 to surface states. Our measurements with He I and He II radiations, however, gave unity as the value of K, where K is defined as $K = \ln(1+R^{II})/\ln(1+R^{I})$, with R^{I} (using He I) and R^{II} (using He II) representing the relative intensities of peaks 2 and 4 compared to that of peaks 1 and 3, indicating that all the peaks arise due to the bulk state. The angle dependence of relative intensities of the peak is probably more diagnostic of a surface state than variation of the relative intensities with the energies of radiations. This is because the photoejected electrons with low kinetic energies feel the effect of reorganisation of the residual electrons and decay of the final states considerably (Fuggle 1981).

In Ce, while peak 1 (figure 1) is due to conduction band emission, there is some doubt (Allen *et al* 1981; Croft *et al* 1981; Steiner *et al* 1977; Baer *et al* 1981) whether peaks 2 or 3 (in figure 1) is due to $4f$ emission. When the surface of Ce is oxidized to form Ce_2O_3 with the $(6s, 5d)^0\ 4f^1$ configuration of Ce, both peaks 1 and 2 vanish, but peak 3 is unaffected, showing unambiguously that peak 3 is due to $4f^1$ state. This observation suggests that peak 2 is in some way connected with the conduction band. Furthermore, peak 2 exhibits resonance photoemission (Gudat *et al* 1981) characteristic of the f-state and we therefore suggest that this feature represents the formation of an electron-hole pair where the hole in the $4f$ level following the photoemission is screened by localizing a conduction electron. This kind of screening is indeed known for deep core levels (Fuggle *et al* 1980). According to our assignment, the energy difference between peaks 2 and 3 ($\sim$1·5 eV) represents the binding energy of the electron-hole pair. Interestingly, peak 2 has a low FWHM compared to peak 3 which is due to unscreened $4f$ emission (table 1). In Yb, peaks 1 and 3 are sharp while 2 and 4 are relatively broad (table 1). The energy separation (1·3 eV) between 1 and 3 is the same as that between 2 and 4, which is equal to the spin-orbit splitting of the $4f^{13}$ final state. By analogy with Ce, we can assign peaks 2 and 4 to the unscreened

Table 1. Positions and FWHM (in eV) of valence band structures in La, Ce and Yb.

Metal	Peak No.	Binding energy	FWHM
La	1	0·4	—
	2	2·1	0·5
	3	3·5	0·7
Ce	1	0·3	—
	2	0·7	0·5
	3	2·2	0·9
Yb	1	1·2	0·3
	2	1·8	0·8
	3	2·4	0·3
	4	3·1	0·8

$4f_{7/2}$ and $4f_{5/2}$ states respectively while peak 1 (or peak 3) corresponds to electron-hole pair formation with the hole in the $4f_{7/2}$ (or $4f_{5/2}$) state. The binding energy of the electron-hole pair in Yb is the energy difference (0·7 eV) between peaks 1 and 2 (or between 3 and 4). As in Ce, we find that the state representing electron-hole pair formation has a smaller FWHM.

The assignment of peak 2 of Ce and of peaks 1 and 3 of Yb as due to electron-hole pair seems quite reasonable as we can rule out the possibility of shake-up processes or surface states. One of the difficulties of attributing peak 3 in the spectrum of Ce (figure 1) to the $4f^1$ emission has been that it would be impossible for Ce to manifest valence fluctuation with such a large energy ($\sim$2·1 eV) of the $4f$ level within the promotional mode. A similar difficulty will arise with Yb as well if peaks 2 and 4 are assigned to the $4f$ level. However, since the electron-hole pair formation is an integral part of $4f$ hole creation, the binding energy of this pair to a large extent compensates for the large excitation energy required for promoting a $4f$ electron.

The case of La is somewhat different from Ce and Yb in that there is no $4f$ population in the ground state, the empty $4f$ level lying $\sim$4 eV above E_F. As mentioned earlier, peak 1 in the spectrum of La (figure 1) is due to the conduction band. Peak 3 is 3·5 eV below E_F; this prompts us to speculate that peak 3 may arise from the promotion of a conduction band electron to the $4f$ level akin to a shake-up satellite accompanying the photoemission from the conduction band. Peak 2 which is narrower than peak 3 (see table 1) can be assigned to electron-hole pair formation with the electron in the $4f$ level; the binding energy of such a pair will then be $\sim$1·4 eV.

It is noteworthy that an extra feature has been noticed in the valence band of Eu in $EuPd_2Si_2$ which the authors have attributed to a surface state (Martensson *et al* 1982). It is possible that the valence band features of Eu may as well be due to electron-hole pair accompanying the unscreened $4f$ emission indicating the presence of a broad $4f$ level. Uranium, with its broad $5f$ level, also seems to exhibit an extra peak in the valence band region (Iwan *et al* 1981). On the basis of theoretical considerations, Liu and Ho (1982) have pointed out that such an electron hole pair formation is indeed possible in Ce. However, the model proposed by these authors is somewhat different. We believe that unscreened $4f$ emission is more probable if the $4f$ level is not highly localized.

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