Selection Rules in Electron-Excited $4d \rightarrow 4f$ Transitions at Intermediate Incident Energies

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Electron-excited $4d^{10} \rightarrow 4d^9 4f$ transitions in clean La metal and tetravalent CeO_2 show systematic deviations from those observed in x-ray absorption. At intermediate primary energies simple selection rules allow a limited range of new singlet excitations, while triplet excitation becomes very prominent as the primary energy approaches threshold. With this technique a complete multiplet analysis of atomiclike core excitations has become possible for the first time.

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Dipole selection rules are well known to apply only in the high-incident-energy, low-momentum-transfer regime for electron-excited transitions, but it is difficult to isolate optically nonallowed transitions for electron scattering in solids. At low and intermediate primary energies in reflection mode it is crucial to be able to distinguish surface features, which are emphasized as the mean free path of incident electrons is reduced, from intrinsic energy dependence in the scattering cross sections. In this Letter we account for spectacular variations in the core electron-energy-loss spectra of elemental La and tetravalent Ce by successive breakdowns of optical selection rules as the energy of the exciting primary electrons is reduced: These give the first confirmation of pseudo selection rules in the intermediate energy regime.

There has been intense interest in photoexcitation studies of $4d \rightarrow nf, \epsilon f$ transitions in atoms and solids with $54 \leq Z \leq 72$ in the last decade.[1-6] Ba, La, and tetravalent Ce all undergo $4d^{10} \rightarrow 4d^9 nf, \epsilon f$ transitions characterized by two sharp, but weak, peaks below the ionization threshold, and a broad resonance beyond. The resonance is $^1P_1$ in character, but the actual wave function of the excited electron involves complex configurational mixing of bound and continuum Hartree-Fock average f wave functions.[7,8] The two sharp peaks, corresponding to highly localized trapping in an "inner well" are the $^3P_1$ and $^2D_1$ states, which are weakly photon excited through a small admixture of $^1P_1$ character due to spin-orbit interaction. The preresonance structure of these systems is less complex than for the other rare-earth systems because of their simpler two-electron multiplet structure.

Core electron-energy-loss (CEELS) spectra were measured in approximately specular reflection geometry with a high-resolution concentric hemispherical analyzer under UHV conditions, as in previous studies on rare-earth systems.[9] The full width at half maximum of the elastically reflected primary beam was measured to be ~0.5 eV over the full range of primary energies used. Spectrometer calibration was made against a clean Au reference sample. Clean metal films (with very low contamination levels as monitored by Auger electron spectroscopy) were evaporated from a tungsten coil onto a Mo substrate. Ce was oxidized to the tetravalent state by admitting oxygen into the chamber from a gas dosing system, and then maintaining a stationary oxygen pressure of 10^{-8} Torr during the recording of the spectra. For incident energies in excess of 1.8 keV the sample was biased to an appropriate voltage to allow electron energy analysis to take place below 1.7 keV.

Figure 1 gives the $4d^{10} \rightarrow 4d^9 4f$ core electron-energy-loss spectra of clean La metal for a range of incident electron energies, and compares the loss spectra with x-ray absorption, which agrees with the low-energy partial-yield spectrum in photoemission.[11] In the inset the ratios of the heights of various sharp peaks to the height of the main resonance are plotted against incident primary energy E_p. Since the breadths of all features are approximately independent of primary energy under these experimental conditions, the ratios shown may be thought of as intensity ratios in a relative sense. Note that the electron-loss spectrum at the highest primary energy is markedly different from the photon absorption spectrum in the region of the sharp

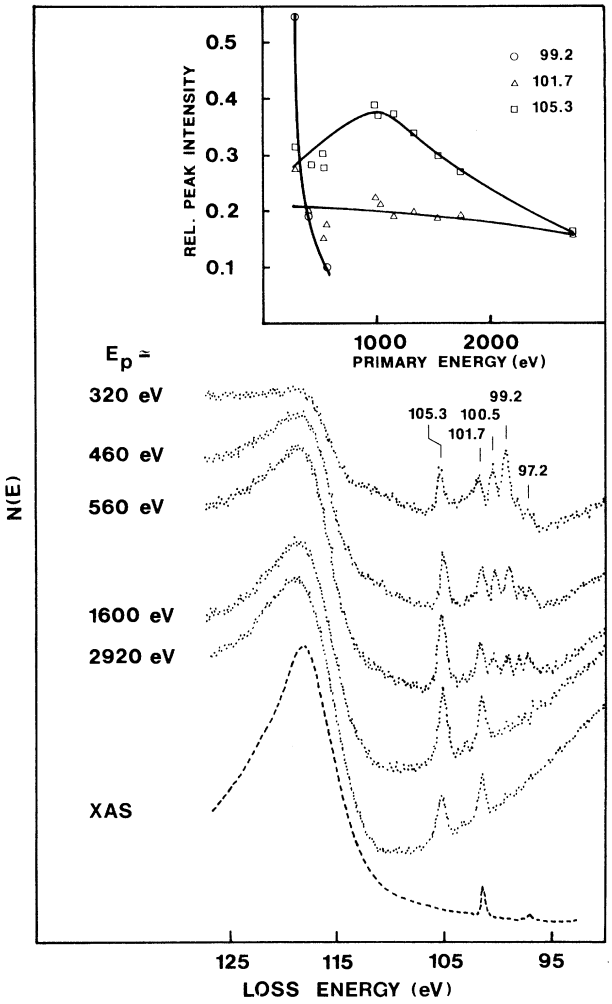

FIG. 1. $4d \rightarrow 4f$ excitations of clean La in CEELS for various primary energies E_p. An x-ray absorption spectrum is shown for comparison (bottom curve, Ref. 10). The inset displays intensities of the sharp peaks at 99.2, 101.7, and 105.3 eV, normalized to the maximum of the main resonance, as a function of E_p.

peaks, but agrees well in the broad resonance. Figure 2 shows corresponding electron-energy-loss spectra for Ce^{4+} in CeO_2, emphasizing the strong similarity of these effects in the two isoelectronic systems.

In this Letter we show that these systematic deviations between the electron-loss spectra and the x-ray absorption spectra may be explained by breakdown of dipole selection rules in two stages as follows: (1) At intermediate energies ($E_p \gtrsim 1$ keV) a restricted set of additional singlet excitations is weakly allowed according to selection rules previously suggested by Goddard *et al.*[12]; (2) at low energies ($E_p \lesssim 500$ eV) triplet excitations give rise to many new components in

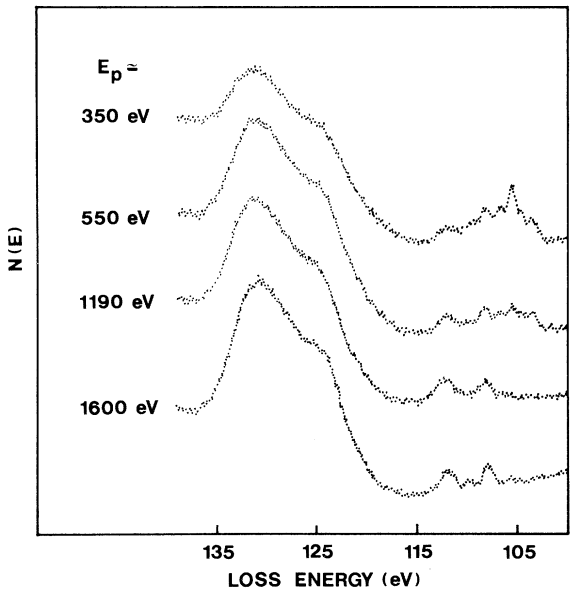

FIG. 2. CEELS of $4d \rightarrow 4f$ excitations of Ce^{4+} in CeO_2.

the spectrum.

The possible final-state multiplets within LS coupling are $^{1,3}P$, $^{1,3}D$, $^{1,3}F$, $^{1,3}G$, and $^{1,3}H$ with the ^1P at highest energy because of strong exchange coupling. Spin-orbit splitting is quite small (± 0.5 eV) and will not radically alter the LS-coupled energy splittings.[8] Term-dependent Hartree-Fock calculations[13] show that all the multiplets apart from ^1P are "collapsed" into the inner well. Within LS coupling the triplets can only be excited by electron exchange, a process whose cross-section peaks sharply near threshold and falls off approximately as E_p^{-3} far from threshold.[14] Apart from $^3P_1$ and $^3D_1$, which have some admixture of dipole-allowed singlet, the remaining three triplets should be very weak at high E_p, and should then rise sharply in intensity as E_p decreases towards threshold. This is exactly the behavior of the peaks at 97.2, 99.2, and 100.5 eV. The intensity versus E_p plot for the 99.2-eV peak gives some quantitative support for triplet assignments. Furthermore multiplet splitting calculations using the term-dependent F^k and G^k parameters of Clark and Lucatorto[13] confirm that the triplets ^3P, ^3H, ^3D, and ^3F occur in the appropriate 97–102 eV region (Table I).

Singlet excitation does not require exchange between incident and target electron, and nondipole processes may continue to be excited at much higher energy than for triplets.[14] However, when the primary energy is in excess of 1 keV only

TABLE I. Relative energies of the highly localized multiplets of $3d^9 4f^1$ in La in LS coupling, compared to the experimental peak energies.

Multiplets	LS-coupling relative energies[a] (eV)	Experimental peak energies (eV) Relative	Absolute
^1F	8.4	8.1	105.3
$^1G, ^3G$	6.2	6.1	103.3
$^3D, ^1D, ^3F, ^1H$	4.5–4.6	3.3–4.5	100.5–101.7
^3H	2.7	2.0	99.2
^3P	0	0	97.2

[a]Obtained with term-dependent Coulomb and exchange parameters (Ref. 13). Results differ by ~ 0.1 eV from those obtained from the term-independent parameters of Radtke (Ref. 15).

two peaks at 105.3 and 101.7 eV in La are clearly observed. Although calculations of the expected relative intensities of these multiplets are very difficult, the intensity variation found here forms an important test for the group-theoretical selection rules for electron-impact spectroscopy of Goddard *et al.*[12] Above 1 keV ($\gtrsim 10$ times threshold) the scattering will be strongly forward biased, and axial symmetry will approximately characterize the collision. For an axial transition $L_i + p_i + L_f + p_f$ must be even, where L_i (p_i) and L_f (p_f) are the initial- and final-state angular momenta (parities), respectively. Although the detector does not exclusively accept forward inelastic scattering events, such processes will dominate at reasonably high energies so that the ^1F and ^1H multiplets will be preferentially excited to supplement the main $^1P_1$ transition and the very weakly dipole-allowed ^3P and ^3D excitations. The calculations presented in Table I show that the ^1H state is close to being degenerate with the dipole-allowed ^3D state, and the ^1F state is well separated to higher energy. We therefore assign the 105.3-eV loss to ^1F excitation and the 101.7-eV loss to ^1H accompanied by a small contribution of dipole-allowed ^3D. As E_p is lowered, and forward scattering becomes less dominant, further singlet excitations will contribute along with the triplet excitations. There is now very good agreement between the relative multiplet energies for theory and experiment if it is remembered that spin-oribt splitting will modify (± 0.5 eV) the level structure. The intensities of the ^1F and $^1H(^3D)$ losses vary much more weakly with primary energy than for triplets as is expected within the Born-Bethe approximation.[14] Trivalent Ce and Gd[16] show very similar effects, but with a more complex multiplet pattern, and this is consistent with earlier observations of anomalous behavior in the rare-earth systems by Borovskii and Komarov.[17]

We may note that the strong primary energy dependence in the electron loss spectra described here can be satisfactorily explained within a single configurational description, and there is no need to invoke dynamical screening mechanisms of the type invoked by Kanski and Wendin[18] for $3d$ losses. Although the nondipole excitation effects outlined in this Letter will be less easy to isolate in systems other than the rare-earth systems, they will nevertheless be present, and for example, triplet excitation will be an important contributing factor to effects resulting from variation of the primary energy on electron losses of transition metals.[19]

In summary, we have isolated nondipole excitations in the $4d \rightarrow 4f$ loss spectra of solid La and tetravalent Ce. We have shown that the breakdown of dipole selection rules takes place in stages with selection rules for singlet excitations important at intermediate energies, and triplets increasing rapidly in intensity near threshold. Although the breakdown of dipole selection rules has previously been demonstrated, e.g., for large momentum transfers in transmission-electron energy-loss experiments,[20,21] it has never before been possible to monitor the energies and intensity variations in each multiplet of such a complex manifold of states. The pattern revealed here will lie hidden amid overlapping features in many systems, and the work presented here will be a guide to the identification of a wide range of excitations that have thus far not been clearly isolated.

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