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Multiplet effects and breakdown of dipole selection rules in the $3d \rightarrow 4f$ core-electron-energy-loss spectra of La, Ce, and Gd

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Electron-energy-loss spectra of La, Ce, and Gd in the region of the $3d^{10}4f^{n} \rightarrow 3d^{9}4f^{n+1}$ excitations show doublet structures associated with each spin-orbit component. The relative intensities of the structures vary systematically with excitation energy, the lower-energy component being emphasized at lower primary energies. The effects are interpreted in terms of the multiplet structure of the final state coupled to progressive breakdown of optical selection rules with decreasing energy of the exciting beam.

Recently, Kanski and Nilsson (KN)[1] and Kanski and Wendin (KW)[2] have noted an anomalous dependence of the $3d^{10}4f^{n} \rightarrow 3d^{9}4f^{n+1}$ core-electron-energy-loss spectra of Ba, La, and Ce on incident primary energy. At high incident energy the loss structure in Ba and La is characterized by strong $3d^{10} \rightarrow 3d_{3/2}4f(^1P_1)$ and $3d_{5/2}4f(^3D_1, {}^3P_1)$ excitations as seen in x-ray absorption, but as the primary energy is lowered towards threshold further peaks 2–3 eV below the main losses grow in intensity. Kanski and Wendin[2] attribute the behavior to coherence between excitation and decay of a higher $3d^{9}4f^{N+2}$ state such that the primary electron can gain energy from the system after the excited electron state decays, for example, to a $3d^{10}4f^{1}$ state in Ba and La, several eV above the ground state. The extra peaks have also been seen in x-ray emission when the incident electron primary energy is ~50 eV above threshold. It is, however, surprising that such coherent behavior between the ingoing electron and the excited electron persists to exit energies of 500 eV or more in the electron-loss experiment.

Esteva *et al.*[3] have studied the relation between the $3d$ x-ray absorption spectrum and the $3d$ x-ray photoemission spectrum in La and Ce: in order to understand the discrepancies between excitation energies to corresponding configurations it is necessary to invoke final-state multiplet structure in conjunction with different selection rules for the two processes.

This work will attempt to show how this final-state multiplet structure, coupled with progressive breakdown of dipole selection rules as the incident primary energy is reduced, can account for the observed primary energy dependence in electron loss. We present electron-energy-loss data for $3d \rightarrow 4f$ excitation in La, Ce, and Gd. The data for La and Ce agree well with KN and KW, but are at higher-energy resolution; this proves important in understanding the loss mechanism. No $3d \rightarrow 4f$ Gd losses have previously been published. In addition, an unsuccessful attempt was made to observe electron emission from

$$3d^{9}4f^{2} \rightarrow 3d^{10}4f^{0} + e^{-}$$

direct recombination in La, that should be present if a $3d^{9}4f^{2}$ intermediate state can indeed be excited in electron loss, as suggested by KW.

Electron-energy-loss spectra were measured in approximately specular reflection geometry with a concentric hemispherical analyzer as in previous studies on rare-earth systems.[4] The full width at half maximum (FWHM) 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. The La, Ce, and Gd films were evaporated from a tungsten coil onto Mo substrates, and surface cleanliness was monitored by Auger spectroscopy.

Figure 1 compares the $3d \rightarrow 4f$ loss spectra of La for primary energies varying from about 200 eV above threshold to approximately 2 keV. It is not possible to go closer to threshold in this experiment due to the masking of losses by emission from Auger channels such as $N_{45}O_{23}O_{23}$ and $N_{23}N_{45}O_{23}$. Below the loss spectra the $3d^{9}4f^{1}$ multiplet structure of Esteva *et al.*[3] is shown. A spectrum of oxidized La is also included in Fig. 1. The strong similarity between the clean metal and oxidized metal spectra confirms that the losses correspond to atomiclike excitations. Figure 2 gives the corresponding loss data for clean Ce and Gd.

The case of La is by far the simplest to analyze because the multiplet structure of the $3d^{9}4f$ two-particle configuration is less complex than the three- and nine-particle configurations of Ce and Gd. Within j-j coupling there are only three $3d^{9}4f^{1}$ states having $J=1$; of these one $(^3P_1)$ has very low oscilla-

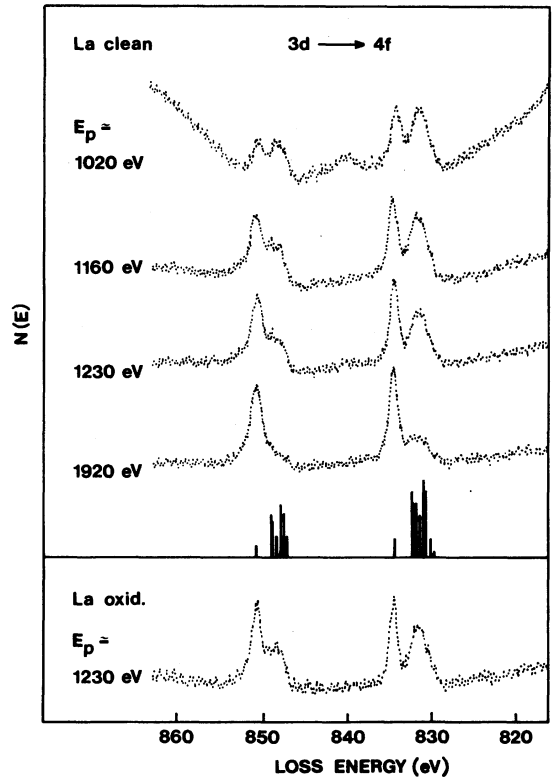

FIG. 1. $3d \rightarrow 4f$ electron-energy-loss spectra of La as a function of primary energy E_p. The $3d^9 4f^1$ multiplet structure is shown in the bar diagram as calculated in Ref. 3. A spectrum of oxidized La is also included for comparison (bottom curve).

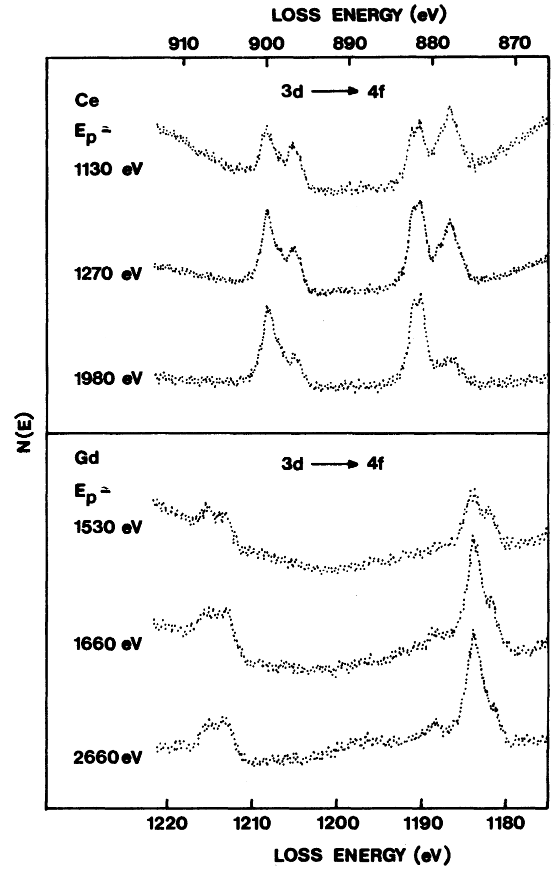

FIG. 2. Electron-energy-loss spectra of $3d \rightarrow 4f$ excitations in Ce and Gd for various primary energies.

tor strength,[5,6] while the $^1P_1$ and $^3D_1$ states may be loosely associated with absorption, leaving holes in $3d_{3/2}$ and $3d_{5/2}$ states. The calculations of Esteva *et al.*[3] reveal a cluster of additional $J \neq 1$ multiplets between 2 and 3.5 eV below each main dipole-allowed peak, i.e., just in the energy region where the extra energy-loss features are observed. It is well known that electron excitation does not obey dipole selection rules except in the high-energy low momentum transfer limit, and so these states are accessible with electron beam excitation. In simple systems such as excitation in He,[7] it has been shown that individual nondipole excitations may have comparable cross sections to dipole excitations for incident energies less than or of the order of twice the threshold energy, but little such data are available for inner-shell excitation.

In the geometry of this experiment small-angle inelastic events are emphasized, and at high incident energies the optically allowed final-state multiplets will dominate the spectrum; but as the primary energy is lowered nondipole excitation will increase in importance. This agrees with the steady increase in intensity of the peaks on the low-energy side of the main losses. Furthermore, the lower-energy peaks are significantly broader than the main peaks (FWHM 2.5 eV compared to 1.3 eV), consistent with these features being due to a manifold of $J \neq 1$ multiplets, while the main peak is associated with a single multiplet, and has a breadth determined solely by core lifetime broadening. The extra broadening is comparable to what might be expected from convoluting the appropriate lifetime-broadened profile with δ functions having $(2J+1)$ multiplicity weighting, indicating that all (or at least most) multiplets gain substantial cross section at the lower primary energies. For the case of LS coupling, which is approximately valid for $4d \rightarrow 4f$ excitations, it has been shown[8] that a restricted set of singlets retains a significant scattering cross section up to relatively high energy; but that as the primary energy approaches threshold strong excitation of all triplets becomes important. In j-j coupling the isolation of multiplets, which require electron exchange to be strongly excited, is much less clear, but certainly all multiplets will be accessible, most with substantial cross section.

In suggesting that multiplet effects are mainly responsible for the primary energy dependence in the

$3d$ loss spectra of La and Ce, we must also account for extra peaks seen in x-ray emission at primary energies ~ 50 eV above threshold.[1] Under these conditions multiplicity considerations will probably cause the nondipole terms to *dominate* over the dipole terms, yet the observed x-ray satellites are weaker than for the electron-loss spectra at ~ 200 eV above threshold. Dipole emission rules will inhibit direct

$$3d^9 4f^1 (J \neq 1) \rightarrow 3d^{10} 4f^0$$

transitions, but crystal-field-assisted and phonon-assisted transitions may be responsible for the emission in this region. It is interesting to note that no satellites are observed in soft x-ray emission at primary energies 300 eV above threshold, an energy at which electron loss shows strong satellites.[1]

One of the arguments put forward by KW for dynamical screening effects was that the multiplet structure would differ for Ba, La, and Ce, while the observed effects show very similar behavior. While Ba and La both have mainly $3d^9 4f^1$ final states, Ce would dominately have the $3d^9 4f^2$ configuration. There are then 24 *dipole-allowed* components, but only a small number of these carry significant oscillator strength.[6] For $3d_{5/2}4f^2$ the important components range over less than 1.5 eV, while for $3d_{3/2}4f^2$ they span 1.8 eV, leading to some structure in the x-ray absorption spectrum. Assuming a $3d^{10}4f_{5/2}$ ground state for Ce the appropriate dipole final states have J values $\frac{3}{2}$ to $\frac{7}{2}$, compared to a possible range $J = \frac{1}{2} - \frac{17}{2}$. For the loss phenomenon to be similar in La and Ce it is merely required that the centroid of the multiplet structure is lower than the centroid of the dipole components, as is needed to explain the x-ray photoemission spectroscopy spectra.[3] High spin multiplicity, high-J components will tend to be low in energy due to favorable exchange coupling, and this trend is supported by the detailed calculations of Spector *et al.*[9] for the $3d^9 4f^2$ states of Pr. The Ce $3d$ loss spectrum (Fig. 2) also supports this pattern, which might be expected to hold for the lower elements in the rare-earth series. However, the Gd $3d$ loss spectrum also shows distinct enhancement on the low-energy side of the main $3d$ loss peaks at low primary energies, suggesting a consistent trend along a substantial part of the rare-earth series.

Attempts were made to confirm the presence of a possible $3d^9 4f^2$ state, as suggested by KW in La, by monitoring electron emission in the region of the direct-recombination transitions

$$3d^9 4f^2 \rightarrow 3d^{10} 4f^0 + e \ .$$

Since the final state is the ground state, electron emission should occur at the energies of the anomalous loss peak excitations. No such emission was found. In contrast, weak emission at energies corresponding to the above transition were observed for Ce, consistent with decay of the conventional $3d^9 4f^2$ excited state by direct recombination. These observations will be reported in more detail elsewhere, but in the context of this paper they give no support for

$$3d^{10} 4f^n V^m \rightarrow 3d^9 4f^{n+2} V^{m-1}$$

transitions close to threshold (m is the valence electron count).

The multiplet interpretation of the primary energy dependence of the $3d$ core-electron-energy-loss spectra of La, Ce, and Gd presented here is further supported by strong multiplet effects observed in the $4d \rightarrow 4f$ excitations of La and Ce,[8] in which the energy dependence of the individual multiplets can be measured and interpreted, and in the $4p$ loss spectra of La, Ce, and Gd,[10] where more complicated breakdown of the one-electron approximation occurs.

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