Direct-recombination electron emission from $3d$ excitation in Ce

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The first observation of $3d$ direct-recombination electron emission in the rare earths is reported. The $3d^9 4f^2$ state of Ce is induced by electron excitation, and $3d^9 4f^2 \rightarrow 3d^{10} 4f^0 + \epsilon l$ electron emission is observed at energies above the main Auger decay channels. The interpretation is confirmed by comparison with emission from La, in which such processes cannot occur. CeO_2 behaves in a similar manner to Ce metal, supporting suggestions of a $4f^2$ configuration contribution in the final state following $3d$ excitation.

In the rare earths both x-ray- and electron-induced excitations from $3d$ and $4d$ levels to empty $4f$ states are known to be highly localized in character. In the case of $4d$ excitation the presence of final-state multiplet structure characteristic of $4d^{10} 4f^n \rightarrow 4d^9 4f^{n+1}$ transitions is well established. For $3d$ excitation the multiplet structure is somewhat less prominent, but atomic behavior can clearly be inferred from the fact that the absorption energies are *less* than the $3d$ x-ray photoelectron spectroscopy (XPS) energies and are insensitive to environment for a given $4f$ population.[1] Electron-energy-loss spectroscopy reveals additional $3d$ excitation structure not observed in x-ray absorption,[2] and Matthew *et al.*[3] have recently interpreted these features as additional $3d^9 4f^{n+1}$ multiplet states which are not dipole allowed.

Atomiclike behavior may be further confirmed by monitoring the decay of the excited state. In the case of $4d$ excitation by monochromatic synchrotron-radiation resonant enhancement of photoemission from weakly bound electron states is observed, corresponding to direct-recombination processes such as

$$\begin{aligned} 4d^9 5s^2 5p^6 4f^{n+1} V &\rightarrow 4d^{10} 5s^2 5p^6 4f^{n-1} V + \epsilon l \\ &\rightarrow 4d^{10} 5s^2 5p^6 4f^n V^{-1} + \epsilon l \\ &\rightarrow 4d^{10} 5s^2 5p^5 4f^n V + \epsilon l \\ &\rightarrow 4d^{10} 5s^1 5p^6 4f^n V + \epsilon l \ , \end{aligned} \tag{1}$$

which have been widely observed.[4–6]

Under electron excitation both Auger emission from ionized atoms and direct-recombination emission occur, and Matthew and Girvin[7] have shown that, for reasonably high incident energy, the electron-stimulated emission corresponds to an integral of the photon-stimulated yield over all photon energies, and as a result the direct-recombination yield may become masked by Auger emission in the same energy region. Where the main excitation is significantly above the $4d$ ionization threshold one direct-recombination channel will emit at energies well above the main Auger channel, and direct recombination may then be unambiguously identified,[8–11] conditions that appear to be satisfied on all the rare earths up to Tb. In addition, Hoogewijs *et al.*[12] have recently seen weak resonant electron emission from heavily oxidized La due to

$$4d^9 4f^1 V \rightarrow 4d^{10} 4f^0 V^{-1} \tag{2}$$

direct recombination, with V corresponding here to the mainly O $2p$ valence band, i.e., an interatomic direct-recombination process.

For $3d$ excitations resonant photoemission is much more difficult because of the higher binding energy involved, so that Esteva *et al.*[13] have only been able to measure the electron yield as a function of photon energy, and to correlate the results with $3d$ absorption in La and Gd. Chamberlain *et al.*[14] and Connerade and Karnatak[15] have, however, observed resonant $3d^9 4f^{n+1} \rightarrow 3d^{10} 4f^n + h\nu$ x-ray emission suggesting that the probability of direct recombination is significant. Under electron excitation $3d$ direct-recombination emission is even less easily separated from Auger emission than in the case of $4d$ excitation, because the $3d \rightarrow 4f$ transition energies are generally *below* the corresponding $3d$ ionization thresholds. Ce is a potential exception to this pattern. Assuming a dominantly $4f^1$ configuration for the ground state of Ce metal (γ phase) it should be possible to observe the direct-recombination (DR) channel

$$3d^9 4f^2 \rightarrow 3d^{10} 4f^0 + \epsilon l \tag{3}$$

because in that case there is no comparable Auger channel. The predicted emission energies $E^{\mathrm{DR}}_{3/2\,(5/2)}$ are

$$E^{\mathrm{DR}}_{3/2\,(5/2)} = E_{3/2\,(5/2)} - W_{4f} \ ,$$

where $E_{3/2\,(5/2)}$ are the main dipole-allowed $3d_{3/2}$ and $3d_{5/2}$ excitation energies observed for relatively high incident electron energies, and W_{4f} is the $4f$ binding energy (see Table I). Direct-recombination processes of type

$$3d^9 4f^2 V \rightarrow 3d^{10} 4f^1 V^{-1} + \epsilon l \tag{4}$$

are also possible, and will be in competition with Auger transitions of type

$$3d^9 4f^1 V \rightarrow 3d^{10} 4f^0 V^{-1} + \epsilon l \quad (5)$$

$$\rightarrow 3d^{10} 4f^1 V^{-2} + \epsilon l \quad (6)$$

in a similar energy region. Assuming zero effective Coulomb interaction the predicted Auger energies of these processes are then ~ 2 eV below the $3d_{3/2\,(5/2)}$ ionization energies (Table I). Although the matrix elements for such transitions involving one or more conduction electrons are likely to be smaller than for the pure $4f$ direct-recombination channel, it is necessary to eliminate these possibilities empirically. One is able to achieve such discrimination by comparing emission at electron kinetic energies just below the $3d$ ionization energies both in Ce and La. In Ce channels Eqs. (3)—(6) are all open, while in La the process we are investigating (3) is absent, and process (5) corresponds to a direct-recombination channel, which accompanies the Auger channel

$$3d^9 4f^0 V \rightarrow 3d^{10} 4f^0 V^{-2} + \epsilon l \ . \quad (7)$$

A potential problem in the interpretation of such exper-

TABLE I. Estimates of direct-recombination emission energies and Auger energies for elemental Ce and La from empirical binding-energy and excitation energy data.

Excitation energies[a]		Energy (eV)		
		La ($n=0$)	Ce ($n=1$)	
$3d^{10}4f^n \rightarrow (3d^9)_{5/2}4f^{n+1}$		835	882	
$\rightarrow (3d^9)_{3/2}4f^{n+1}$		851	900	
Binding energies XPS[b]				
V		0-1	0-1	
$4f$			2[c]	
$4d$		105	109	
$3d_{5/2}$		836.1	884.2	
$3d_{3/2}$		852.9	902.7	
U_{eff} $4d$-$4f$ (estimated)		6	6	
$4d$-V (estimated)		0	0	
Appearance potential spectroscopy				
$3d^{10}+e \rightarrow (3d^9)_{5/2}4f^2$		837[d]		
$\rightarrow (3d^9)_{3/2}4f^2$		853[e]		
				Ce
Direct recombination			Calculated	Experimental
$(3d^9)_{3/2}4d^{10}4f^{n+1}V$	$\rightarrow 3d^{10}4d^{10}4f^{n-1}V$		898	896
	$\rightarrow 3d^{10}4d^{10}4f^nV^{-1}$	850	899	
	$\rightarrow 3d^{10}4d^94f^nV$	746	791	
$(3d^9)_{5/2}4d^{10}4f^{n+1}V$	$\rightarrow 3d^{10}4d^{10}4f^{n-1}V$		880	880
	$\rightarrow 3d^{10}4d^{10}4f^nV^{-1}$	834	881	
	$\rightarrow 3d^{10}4d^94f^nV$	730	773	
Auger			Calculated	Experimental
$M_4N_{67}V$			900	
M_4VV		852	901	
$M_4N_{45}N_{67}$			787	788
$M_4N_{45}V$		747[f]	793[f]	
$M_4N_{45}O_{23}$		726[f]	768[f]	770
$M_4N_{45}O_1$		708	752	754
$M_5N_{67}V$			881	
M_5VV		834	882	
$M_5N_{45}N_{67}$			768	770
$M_5N_{45}V$		729	774	
$M_5N_{45}O_{23}$		709[f]	750[f]	754
$M_5N_{45}O_1$		691[f]	734[f]	739

[a]Reference 11.
[b]Reference 22.
[c]Reference 23.
[d]Reference 2 and 19.
[e]Estimated from Ref. 2 and the $3d$ spin-orbit splitting.
[f]Estimates of Ref. 24.

iments is ambiguity in the number of 4f electrons particularly in the excited state. Fuggle *et al.*[16] have shown the importance of this phenomenon in x-ray absorption of rare-earth alloys; in elemental metals it is not significant, but in CeO_2 we shall show that similar effects occur.

The experimental setup to investigate these effects is as discussed by Matthew *et al.*[10] in studying 4d direct recombination in Ce. The electron-emission spectra were recorded under UHV conditions by a concentric hemispherical analyzer with energy resolution ~ 0.5 eV, and sample Fermi-level reference. A linear background has been subtracted from the spectra shown. Clean La and Ce were evaporated from a tungsten coil on the Mo substrates under ambient pressures $< 10^{-10}$ Torr, the pressure rising to $\leq 10^{-9}$ Torr under evaporation. No impurity Auger signals were detectable on freshly evaporated films. Oxidation to the tetravalent CeO_2 state was achieved by prolonged dosage of O_2 with a stationary O_2 pressure of $\sim 10^{-8}$ Torr maintained in the spectrometer chamber during spectral accumulation. The resulting oxide phase was unambiguously identified as CeO_2-like by its 4d excitation spectrum.[17]

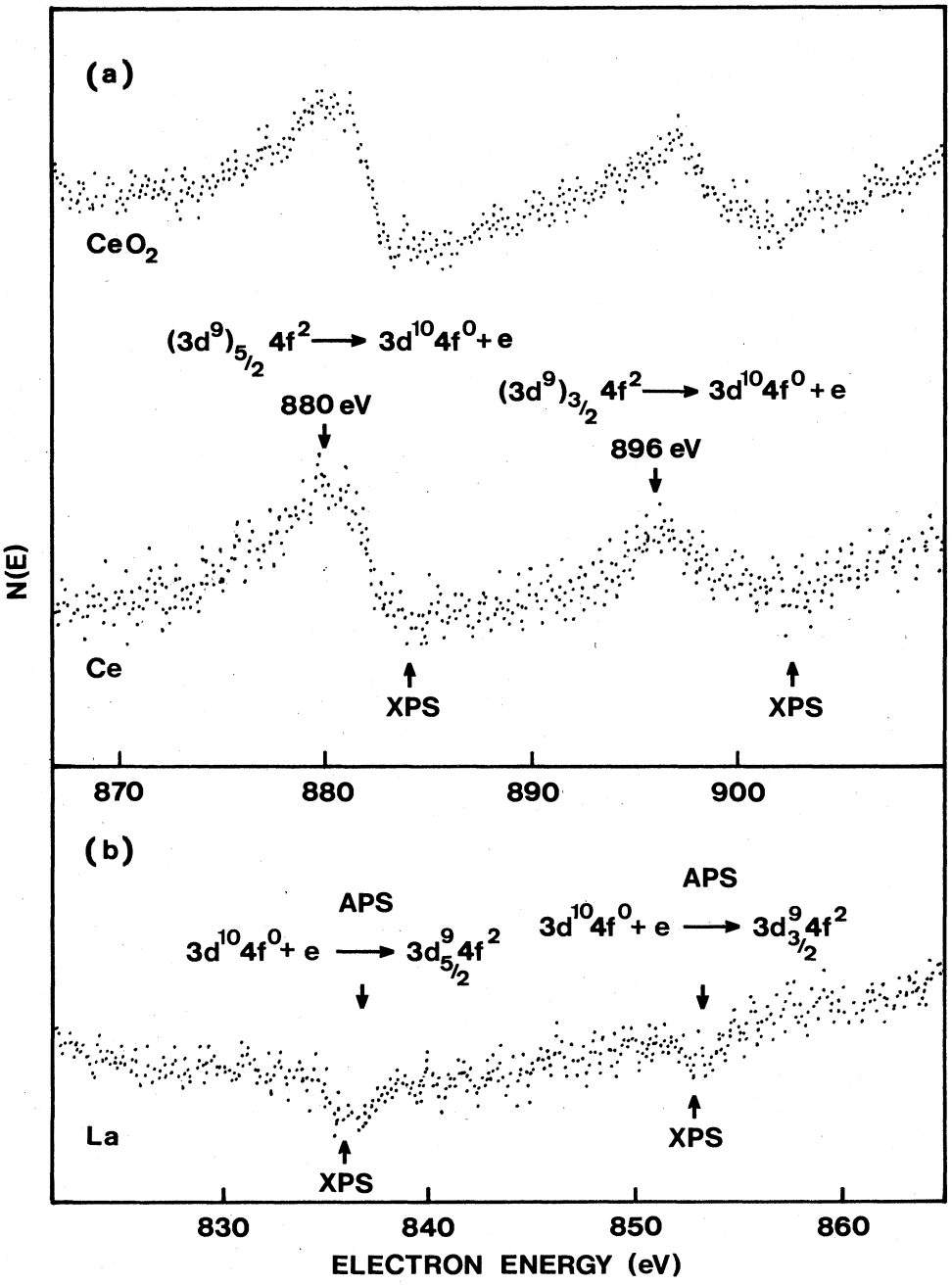

FIG. 1. Electron emission $N(E)$ following electron-induced excitation in the kinetic energy region of the $3d_{3/2}$ and $3d_{5/2}$ binding energies. (a) clean Ce metal and CeO_2; (b) clean La—note the dips rather than peaks in the electron-energy distribution.

Figure 1 compares electron emission from clean Ce and La in the kinetic energy range around their respective $3d$ binding energies. In the case of clean Ce metal [Fig. 1(a)] weak emission is observed near the $3d^9 4f^2 \rightarrow 3d^{10} 4f^0$ direct-recombination emission energies, but for La no corresponding features are found [Fig. 1(b)]. Instead very small dips in emission are seen just *above* the $3d_{3/2}$ and $3d_{5/2}$ ionization thresholds: This probably corresponds to a "disappearance-potential" effect[18] in which electrons leaving the solid are preferentially removed from the background at energies corresponding to the appearance-potential excitations seen by Kańaski *et al.*[2,19] The Auger processes of type $3d^9 4f^1 V \rightarrow 3d^{10} 4f^0 V^{-1}$, which are possible for Ce, but can occur as direct recombination in La, are predicted to occur at slightly higher energies than for the $3d^9 4f^2 \rightarrow 3d^{10} 4f^0$ direct-recombination channel (Table I), but appear not to be of importance. This is consistent with the trend noted by Gerken and co-workers[6,9] for $4d$ resonant photoemission, where conduction-band-electron contributions to the partial ionization cross sections were substantially less than for the $4f$ channel. The contrast in behavior of Ce and La appears to confirm that the emission in Ce is mainly due to direct recombination involving only $4f$ electrons.

Figure 1(a) also shows the direct-recombination spectrum of heavily oxidized Ce [in the form of CeO_2 (Ref. 17)]. The strong similarity between clean Ce and CeO_2 is at first sight surprising in that nominally tetravalent Ce (with ground-state configuration mainly $4f^0$) might be expected to behave like La. However, recent studies[17] suggest that the main $3d$ excitation state of CeO_2 may correspond to a $3d^9 4f^2$-like final state through $4f$ screening by $4f$-O_{2p} mixing. The emission from oxidized La (not shown) differs little from the clean metal, so this suggests that $3d$ emission in CeO_2 is not of the same type as the interatomic processes observed in the $4d$ emission of heavily oxidized lanthanum.[12] Further support for this view comes from the similarity of $4d$ emission of Ce metal[10] and CeO_2.[11] The direct-recombination experiment presented here suggests that the state following $3d$ excitation is very different for La and tetravalent Ce, and gives support to the $4f$ screening hypothesis in CeO_2. It should be mentioned that these experiments do not explicitly give information on the ground state of CeO_2, but that they are not inconsistent with recent theoretical descriptions of CeO_2.[20,21]

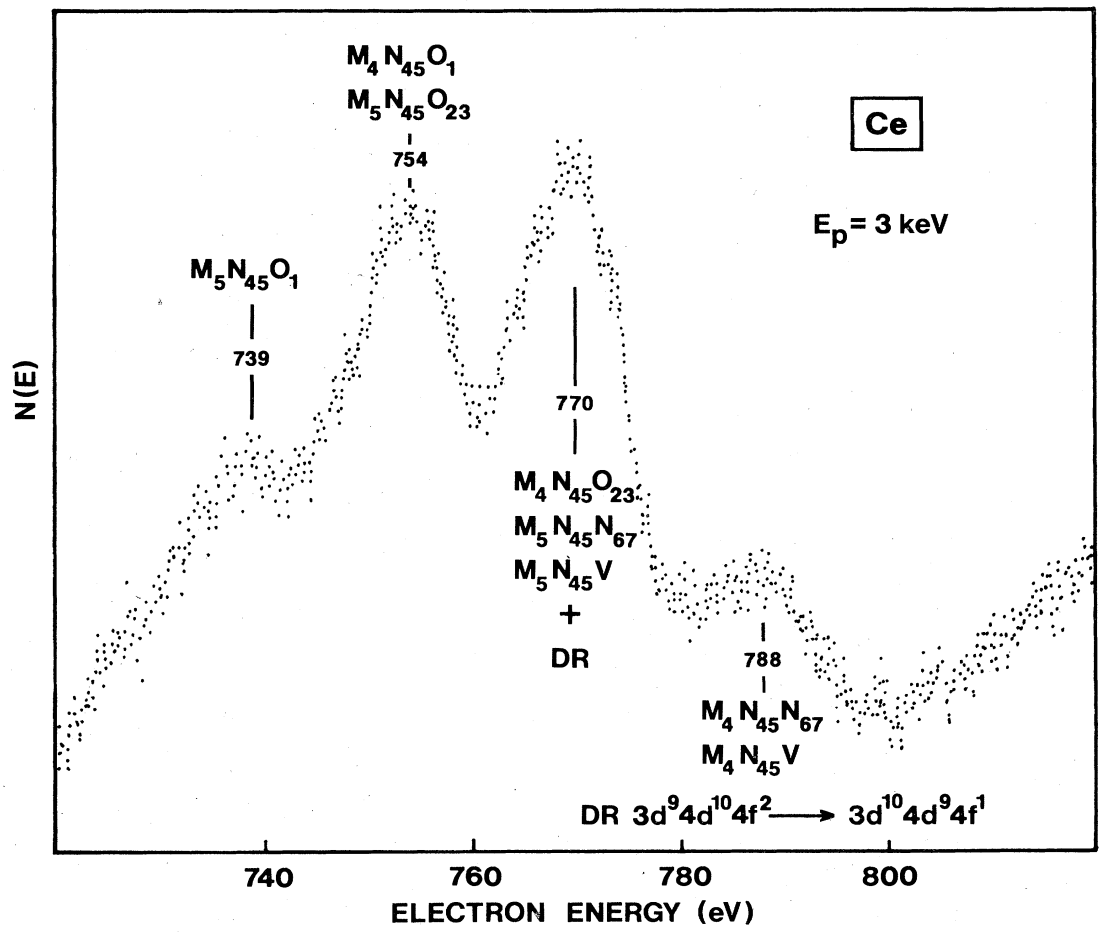

FIG. 2. Auger and direct-recombination electron emission of clean Ce in the region of $M_{4\,(5)}N_{4,5}X$ transitions with $X = (V, 4f, 5p, 5s)$.

The main Auger emission channels following $3d$ ionization in La ($n=0$) and Ce ($n=1$) involve creating a $4d$ hole:

$$3d^9 4d^{10} 5s^2 5p^6 4f^n V \rightarrow 3d^{10} 4d^9 5s^2 5p^6 4f^{n-1} V + \epsilon l \quad (8)$$

$$\rightarrow 3d^{10} 4d^9 5s^2 5p^6 4f^n V^{-1}\ \epsilon l\ , \quad (9)$$

with process (8) absent for La. Given that direct recombination has been isolated above for the case of Ce, it seems likely that direct-recombination emission of type

$$3d^9 4d^{10} 5s^2 5p^6 4f^{n+1} V \rightarrow 3d^{10} 4d^9 5s^2 5p^6 4f^n V + \epsilon l \quad (10)$$

will also occur *both* in La and Ce, along with other channels in which the excited $4f$ electron is a spectator, e.g.,

$$3d^9 4d^{10} 5s^2 5p^6 4f^{n+1} \rightarrow 3d^{10} 4d^9 5s^2 5p^5 4f^{n+1} + \epsilon l\ . \quad (11)$$

Making plausible assumptions about the effective Coulomb interaction (~ 6 eV) between $4d$ and $4f$ electrons, the Auger transitions are predicted to occur at energies very similar to those of competing direct-recombination channels (Table I), and it is not possible to separate clearly the two processes in the observed emission spectrum (Fig. 2). Comparison with the corresponding emission obtained under nonresonant x-ray excitation would be needed to make an unambiguous assignment, but a substantial contribution from direction recombination seems likely. Similarly Auger emission and direct recombination involving $5p$ and $5s$ electrons will overlap.

This investigation highlights the advantages and disadvantages of studying nonradiative de-excitation processes using electron excitation. Much more incident flux is available than for tunable photon sources when the binding energy is >500 eV, but, because electron impact lacks the selective excitation of resonant photon excitation, it is possible to isolate the direct recombination from Auger emission in only a limited number of cases.

In summary, comparison of electron emission following electron-excited $3d$ core-hole creation in La and Ce confirms the presence of weak $3d^9 4f^2 \rightarrow 3d^{10} 4f^0 + \epsilon l$; direct recombination; the $3d$ Auger spectra of Ce and La contains emission from a variety of direct-recombination processes. The work presented here predicts that resonant photoemission should be observable in the $4d$, $5p$, and $4f$ channels in Ce for photon energies corresponding to the $3d$ photoabsorption. Electron-excited direct-recombination emission appears to provide a useful way of distinguishing $4f^1$ and $4f^2$ final configurations, and results for CeO_2 give support for a $3d^9\ 4f^2$ contribution in the excited state.

Note added in proof. Allen *et al.* have recently observed resonant enhancement of $4f$ photoemission at the $3d$ absorption edge of CeAl and $TbCo_2$, i.e., the photon-excited analog of the direct-recombination phenomenon presented here [J. W. Allen, S.-J. Oh, I. Lindau, and L. I. Johansson, Phys. Rev. B **29**, 5927 (1984)].

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