Nature of Resonant Photoemission in Gd

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The phenomenon of resonant photoemission happens when, in addition to a direct photoemission channel, a second indirect channel opens up as the absorption threshold of a core level is crossed. A massive increase in emission cross section can occur, but the nature of the process remains clouded. Using novel magnetic linear dichroism in photoelectron spectroscopy experiments and theoretical calculations, we can now clearly demonstrate that temporal matching of the processes as well as energy matching is a requirement for true "resonant photoemission." [S0031-9007(98)06819-7]

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The photoemission of $4f$ and $5p$ electrons from rare-earth metals and their compounds is strongly enhanced when the photon has just enough energy to excite a $4d$ electron to an unoccupied $4f$ level, leading to a process called "resonant photoemission." (See Fig. 1.) In a generic picture, the indirect channel of the resonant photoemission is interpreted as due to a process where a $4d$ electron in the initial state is first excited to the unoccupied $4f$ level, forming a tightly coupled, bound intermediate state, $4d$ core hole plus $4f$ electrons. Then a decay via autoionization occurs, producing a final state identical to that obtained by a direct photoemission process for the ejected electron [1]. The transition rate is greatly enhanced if the excited state decay is by a (super)-Coster-Kronig [(s)CK] process [2,3]. The key question is whether these processes are coherent or incoherent: Is it truly resonant photoemission or merely the incoherent addition of a second emission channel? Should the overall intensity be treated as a squaring of the sum of the amplitudes (coherent) or summing of the squares of the amplitudes (incoherent)? A true resonant photoemission process should be coherent, involving interference terms between the direct photoemission and indirect photoemission channels. Possibly, incoherence would give rise to the loss of photoemission characteristics in the process, with a domination of Auger-like properties.

To this problem we have applied the new photoelectron spectroscopy technique of magnetic linear dichroism in angular distributions (MLDAD) [4–7]. This technique is related to but distinct from the techniques of magnetic x ray circular dichroism (MXCD) in photoelectron spectroscopy and x ray absorption [8–13]. The key is that while strong MXCD effects in ferromagnets can be observed with photoemission and absorption, the large MLDAD effect in ferromagnets is solely a photoemission, not an absorption-driven, process. This is because the chirality which gives rise to magnetic sensitivity is due to the vectorial configuration in MLDAD as opposed to the

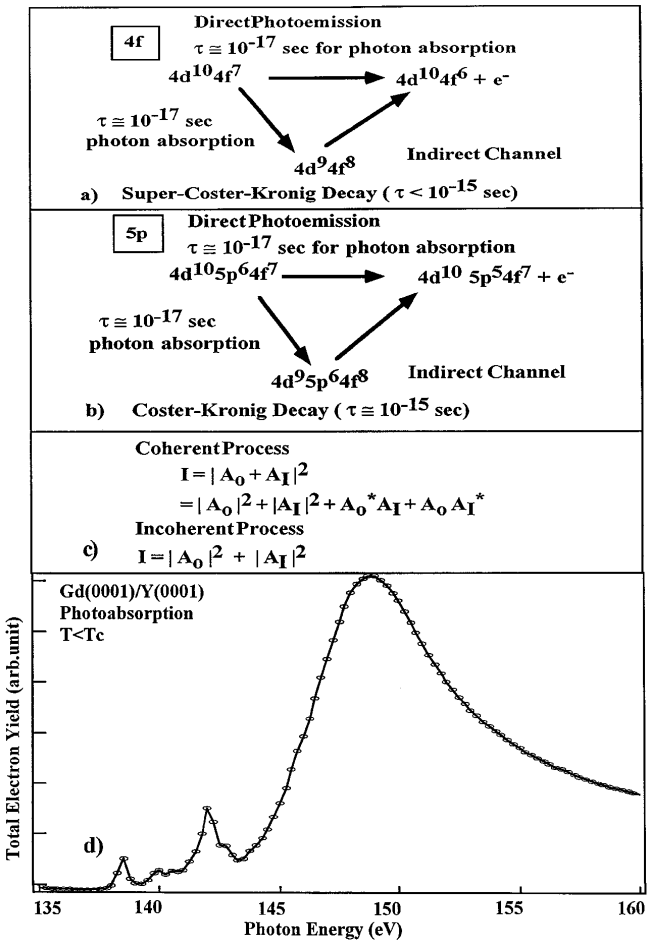

FIG. 1. (a) Schematic diagram of the direct and indirect channels in Gd $4f$ resonant photoemission. Time estimates are based on Refs. [2,3]. (b) Same for Gd $5p$ emission. (c) Comparison of coherent and incoherent additions of channel contributions. A0 (AI) is the direct (indirect) amplitude. (d) The photoabsorption of Gd/Y(0001), near the Gd $4d$ giant resonance. The pre-peak structure occurs between photon energies of 138–144 eV and the giant resonance is present at photon energies above 144 eV.

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intrinsic chirality of circularly polarized x rays in the MXCD techniques [14]. In absorption, where there is an essential averaging over all emission angles, the vectorial chirality is lost. Thus, MLDAD is the ideal measurement to distinguish between photoemission and absorption processes. Angle-resolved photoemission in a magnetic system should show an MLDAD effect: x ray absorption and thus Auger-like emission will show no MLDAD effect. It is this test which we have applied to the resonant photoemission of the Gd$5p$ and Gd$4f$ emissions.

Experimental details can be found elsewhere [15–19]. Theoretical spectra were calculated in intermediate coupling using Cowan's relativistic Hartree-Fock code [20]. Radiative transitions were taken into account to first order and (s)CK transitions to infinite order [21,22]. Line broadening of the photoelectron state and experimental resolution were included by a convolution with a Lorentzian and a Gaussian, respectively. All parameters were taken the same as in Refs. [13,23] and not adapted to suit the current measurements. Interference terms between the photoemission final state continua with orbital quantum numbers $1 - 1$ and $1 + 1$ were fully taken into account as needed for MLDAD [21]. The interference between the direct and resonant channel was included in the $4f$ and excluded in the $5p$ photoemission calculation.

Before considering the photoemission spectra, let us review the photon energy dependence in the resonance regime as evidenced in the x ray absorption spectrum. The total electron yield spectrum from metallic Gd is displayed in Fig. 1(d). There is a group of weak narrow peaks near the $4d$ absorption edge and a broad strong absorption feature at higher energy, around 150 eV, far beyond the $4d$ absorption edge. The strong intermediate coupling resulting from the exchange and Coulomb interaction between $4d$ hole and $4f$ electrons results in multiplet splitting of the $4d^9 4f^8$ configuration [13]. These interactions are very large due to the large radial overlap of the $4d$ and $4f$ wave functions. Features in the $4d$-$4f$ absorption curve arises from the transition from the ground state level of the $4d^{10} 4f^7$ configuration to the numerous intermediate levels of $4d^9 4f^8$ configuration. The broad maximum or giant resonance arises from the rapid decay of the intermediate states from the $4d^9 4f^8$ configuration into a continuum with an ejected electron [24,25]. This type of giant resonance absorption has been observed before in partially filled $5f$, $4f$, and $3d$ metals and their alloys and compounds [1].

Now consider the $4f$ photoemission results. Figure 2 shows a set of angle-resolved energy distribution curves (EDC's) and difference curves. These are at photon energies corresponding to "on" and "off" resonance of the $4d$-$4f$ giant absorption maximum. The resonant photoelectron spectroscopy (REPES) effects are distinguished by comparing photoemission intensity of spectra taken on (150 eV) and off (95 eV) resonance. Experimentally, it is evident that the fairly strong dichroism (a few percent)

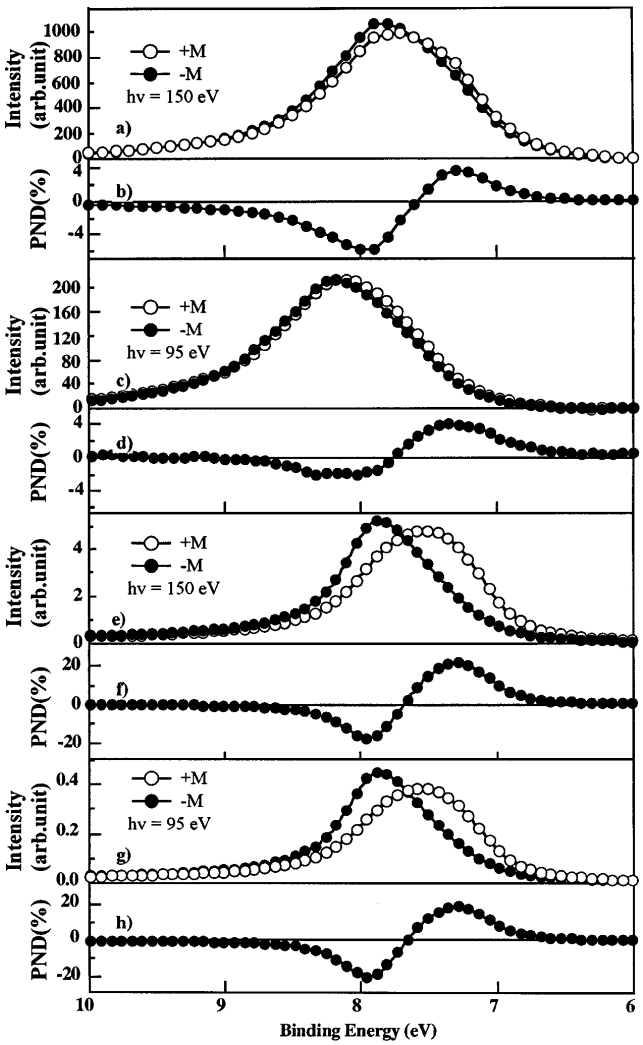

FIG. 2. A series of experimental and theoretical $4f$ photoemission spectra (for the two opposite magnetization directions) and normalized difference curves. (a) $h\nu = 150$ eV, photoelectron spectra, experimental. (b) $h\nu = 150$ eV, photoelectron spectra difference, experimental. (c) $h\nu = 95$ eV, photoelectron spectra, experimental. (d) $h\nu = 95$ eV, photoelectron spectra difference, experimental. (e) $h\nu = 150$ eV, photoelectron spectra, theory. (f) $h\nu = 150$ eV, photoelectron spectra difference, theory. (g) $h\nu = 95$ eV, photoelectron spectra, theory. (h) $h\nu = 95$ eV, photoelectron spectra difference, theory. EDC is energy distribution curve. The spectra in (a), (c), (e), and (g) are EDC's, where the photon energy is held constant and the kinetic energy is scanned. PND stands for peak normalized difference, where the dichroism difference at each binding energy is divided by the sum of the two intensity maxima, one from each pair (following Refs. [4,19]). The photon energy of 150 eV is on resonance and 95 eV is off resonance [cf. Fig. 1(d)]. The relative intensities of the experimental curves were determined by normalizing to the valence band intensities and then correcting for the valence band cross sections. (See Refs. [19,36].)

in the Gd $4f$ peak photoemission intensity persists on and off resonance, despite the fivefold increase in signal size in going from $h\nu = 95$ eV to $h\nu = 150$ eV. This behavior is also seen in the theoretical spectra in Figs. 2(e) and

2(g). Here a tenfold increase in intensity at resonance and a 20% dichroism is predicted. The REPES is caused by the constructive interference [Fig. 1(a)] between the direct PE channel and the indirect photoemission channel [21]. Our observation of the retention of an MLDAD effect in RESPES directly confirms that this transition must be viewed as a single step process in the case of the Gd $4f$. {Spectra taken over the photon energy range of 142–154 eV show similar but not identical effects [17–19]. The near resemblance of the pairs of theoretical spectra [2(e) and 2(g)] is somewhat accidental [26].} The interference between channels is necessary for the observation of photoemission dichroism in a regime where the indirect channel dominates the total cross section. So this is clearly a coherent process, as illustrated in Fig. 1(c), where cross channel interference is crucial. Our observation of photoemission effects in the $4f$ emission resonance is consistent with earlier related work [12,13,27–30].

Next, let us consider the $5p$ emission shown in Fig. 3. [See Fig. 1(b) for the channel diagram.] Here there is a large dichroism observed off resonance at $h\upsilon = 137$ eV, with a disappearance of any dichroism on resonance ($h\upsilon = 151$ eV). In this case, there is a threefold increase experimentally and a tenfold increase theoretically in the intensity, in going from off resonance to on resonance. Interestingly, the peak normalized differences (PND's) or percentage dichroisms match very well between experiment and theory. Moreover, despite using parameters derived elsewhere [22,23], a very good match is observed between the theoretical and experimental spectra and difference curves, including all of the fine structure in the $5p$ manifold. Over the photon energy range of 138–150 eV, other EDC pairs exhibit similar dichroic differences to that at $h\upsilon = 137$ eV but with strong changes in the shapes of the "raw" EDC spectra and a decrease in the dichroism percentage (PND) as the photon energy moves toward the maximum of the giant resonance [26]. The disappearance correlates with the giant resonance. Here it is clear that the second equation in Fig. 1(c) applies, where the process is incoherent and emission at $h\upsilon = 151$ eV is essentially Auger-like, not a direct photoemission process at all.

This raises a key question: 'Why is the $4f$ emission "photoemissionlike" and the $5p$ emission "Auger-like"?' The answer may lie in the regime of time. The Coster-Kronig decay that occurs in the $5p$ emission occurs on a time scale of about 10^{-15} sec [2]. The super-Coster-Kronig decay of the $4f$ should be significantly faster [2,3]. This would speed up the indirect channel, bringing it nearer to the time duration of x ray absorption ($\tau \leq 10^{-17}$ sec) that dominates the direct photoemission channel. Thus, not only must the energies of the two channels match but also the time duration, in order to observe "true resonant photoemission." (Owing to complications in other systems, e.g., $3d$ transition metal resonant emission, we will restrict our discussion to Gd and the rare earths here [28,31–34].) Now, operating within the constraint that we are discussing only rare-earth resonant emission, can we find a correlation in the parameters used to calculate the theoretical spectra with this simple temporal picture? The required parameters can be obtained directly from Cowan's calculation. However, here starts the first complication from the proposed holistic model. The Gd $4d$ absorption spectrum consists of hundreds of different lines each having different parameters and, therefore, a different coherence. Fortunately, in the case of Gd $4d$ edge they divide globally, and rather nicely, into two different regions (i) the pre-edge peaks and (ii) the giant resonance. We can deduce two things from the parameters: (a) At a given photoemission decay channel, the lifetime of the states in the pre-edge is about 10 to 20 times longer than in the giant resonance. This is due to the differences in (s)CK decay rates, as manifestly demonstrated by the strongly different line widths in the $4d$ absorption spectrum [Fig. 1(d)].

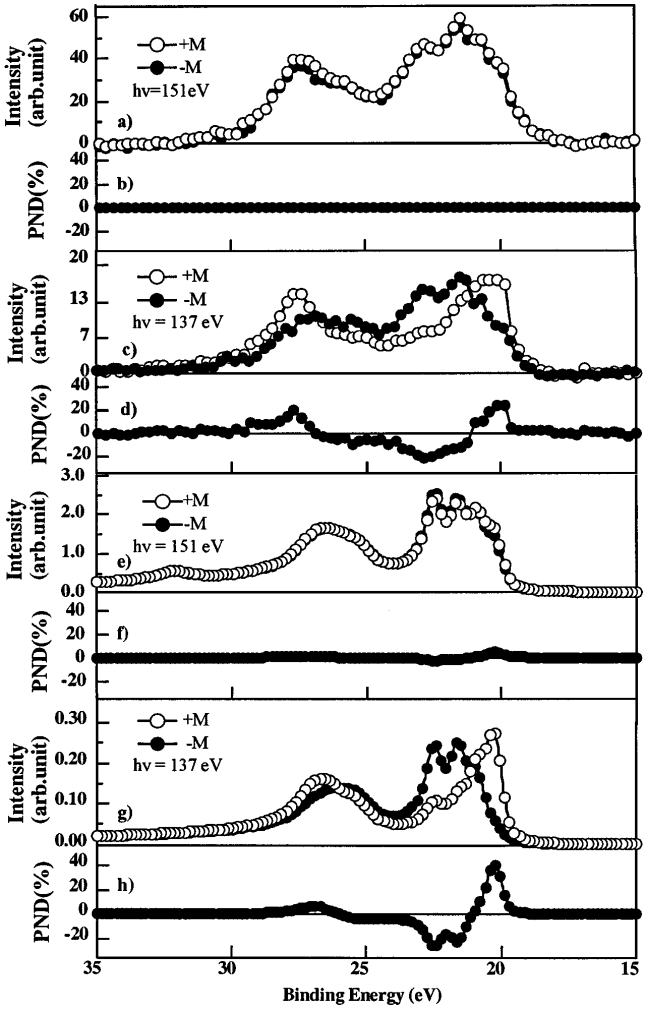

FIG. 3. Analogous to Fig. 2, with photon energies of 151 and 137 eV and looking at $5p$ emission. The photon energy of 151 eV is on resonance and the 137 eV is off resonance [cf. Fig. 1(d)].

(b) For a given absorption state, the (s)CK decay to the $4f$ is about 6 times faster than the CK decay to the $5p$. Thus the $4f$ photoemission is connected to a 6 times shorter lifetime of the $4d$ hole. If resonant photoemission dichroic interference effects occur, they will occur for the $4f$ photoemission decay, but only at the giant resonance (i.e., where the decay is fastest). Outside of the giant resonance regime, the regular photoemission dichroic effects can play a role, as seen in both the Gd $4f$ and $5p$ emission.

We have investigated Gd resonant photoemission with MLDAD. This photoemission technique allows for a direct isolation of photoemission and Auger-like contributions [35]. The Gd $4f$ resonant photoemission is confirmed to be photoemissionlike. The Gd $5p$ resonant emission is shown to be dominated by Auger-like contributions. Temporal channel matching is a requirement for channel interference and the persistence of photoemission effects.

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