Spin-resolved-photoemission-spectroscopy study of the giant resonance in Gd overlayers on Fe(100)

T. Kachel*
Institut für Festkörperforschung, Forschungszentrum Jülich, D-5170 Jülich, Germany

R. Rochow
Institut für Angewandte Physik der Heinrich-Heine-Universität, D-4000 Düsseldorf, Germany

W. Gudat
Berliner Elektronenspeicherringgesellschaft für Synchrotronstrahlung mbH, BESSY, D-1000 Berlin, Germany

R. Jungblut
Institut für Angewandte Physik der Heinrich-Heine-Universität, D-4000 Düsseldorf, Germany

O. Rader* and C. Carbone
Institut für Festkörperforschung, Forschungszentrum Jülich, D-5170 Jülich, Germany
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It is shown that insight into the giant resonance of the lanthanides can be obtained by spin- and energy-resolved photoelectron spectroscopy. Gd has been evaporated onto the Fe(100) surface in the monolayer and submonolayer range of coverage. The spin-dependent electronic structure has been studied by spin-resolved photoemission with photon energies from 70 eV up to the Gd $4d$ threshold. Within the well-known Fano-like giant resonance, the intensity of the Gd $4f$ (^7F) signal shows an enhancement of about a factor of 20. The values of the total spin polarization of the Gd $4f$ (^7F) photoemission peaks on resonance at $h\nu=152$ eV and far away from the threshold at $h\nu=70$ eV are compared. Both values are found to be identical within the experimental error. The results indicate that the amount of non-spin-conserving emission processes in the resonant regime is not increased with respect to the direct photoemission.

I. INTRODUCTION

The giant resonant behavior of valence and core states of rare-earth (RE) atoms has been explored in the late 1970s with use of tunable synchrotron radiation as an excitation source.[1]

For photon energies close to their $4d$ thresholds, RE elements show an extremely large resonant enhancement of their photoabsorption cross sections. Since then several photoemission investigations of this effect have been carried out on RE metals, compounds, and overlayer systems.[2-6] The giant resonance has been studied in order to understand the details of the excitation process, but since it is element and angular momentum specific it also has gained practical importance as a tool to determine the nature of electronic states in RE systems. In most cases the strongly localized $4f$ wave functions of RE atoms carry a nonvanishing total spin momentum that strongly influences the energetics of the electronic states. Very often the interpretations of electronic transitions rely on the assumption of certain spin configurations. Nevertheless, up to now no resonant photoemission data including the explicite measurement of the photoelectron spin polarization has been reported.

In the present work we investigate the effect of the resonant excitation process on the measured spin polarization of the Gd $4f$ electrons and we compare it to the one obtained in direct photoemission. This comparison is of special interest for a number of reasons.

The driving mechanisms of the direct and the resonant emission are not of the same nature. While the direct photoemission process is described by a single dipole matrix element, the simplest description of the resonant excitation consists of a two-step two-level process: a primary optical excitation of a $4d$ electron into an empty $4f$ state followed by a super Coster-Kronig type decay with transfer of the resonance energy to a $4f$ electron. Neglecting the electron spin, the resonant process is usually written as

$$4d^{10}4f^n+h\nu\rightarrow 4d^9 4f^{n+1}\rightarrow 4d^{10}4f^{n-1}+\epsilon l \ ,$$

$h\nu$ being the photon energy and ϵl representing the electron in the continuum state. In resonant photoemission the radiationless decay of the photoexcited intermediate states is described by a Coulomb matrix element.

In the direct photoemission from valence band states the conservation of the photoelectron spin momentum has been assumed to be applicable in most cases.[7] This is

due to the fact that the Russel-Sounders coupling scheme, in which the electron spin is a good quantum number ($\Delta S=0$), often provides a reasonable approximation. In contrast, this argument is not necessarily correct for the giant resonant excitation, since the latter involves the RE $4d$ core levels with relatively large spin-orbit splitting. Rather, the resonant excitations should be described in the intermediate coupling scheme. The consequences are discussed in more detail in Sec. II.

A further motivation to compare the spin polarization in direct and resonant emission is that from spin-resolved Auger spectroscopy the spin polarization of the $O_{4,5}N_{6,7}N_{6,7}$ Auger emission appeared to be considerably smaller than the $O_{4,5}N_{6,7}N_{6,7}$ (^7F) resonant emission,[8] an experimental result that still awaits interpretation.

The magnetic properties of ultrathin Gd layers on Fe(100) are themselves an interesting topic. In previous publications the dependence of the spin polarization of Auger and photoelectrons on overlayer thickness and temperature has been discussed. The spin of the Gd $4f$ electrons couples antiparallel to the spin momentum of the Fe substrate.[9,10] Taborelli *et al.*[9] have determined the Curie temperature of the Gd subsystem for (1 ML Gd)/Fe(100) to be about 800 K, which is strongly enhanced compared to the bulk Curie temperature of Gd ($T_C=293$ K). Carbone and Kisker[10] measured the spin polarized electronic structure of the valence-band region, including the Gd $4f$ electrons for this system. They observed strongly spin polarized Gd $4f$ emission ($P=60\%$ at $T=170$ K) for (1 ML Gd)/Fe(100) at a photon energy $h\nu=70$ eV. The in-plane spin polarization was found to decrease for Gd films thicker than 1 ML. This was attributed to either weakening of the magnetic coupling or a rotation of the spin polarization vector due to perpendicular magnetic anisotropy at higher overlayer thickness. Our new results, concerning the magnetic properties of the system, fully agree with the earlier reported findings and we shall not go into further discussion.

II. DIRECT AND GIANT RESONANT EXCITATION

The possible direct and resonant photoexcitation processes for a RE atom with a half-filled $4f$ subshell are shown in Fig. 1. The diagram gives a very schematic view of the resonant excitation process within a spin-dependent single-particle two-step and two-level picture, previously used also by other authors.[1] However, here the complete set of the possible two-level transitions leading to the ^7F final state is displayed. Every subdiagram contains the $4d$ and the exchange-split $4f$ levels, showing the spin-up electrons on the left and the spin-down electrons on the right. For the resonant processes the white arrows indicate the primary excitation the black ones the transitions of deexcitation. In panel (a) we show processes that conserve the total spin of the two-level system, in panel (b) the non-spin-conserving processes are displayed. All spin-conserving two-level processes with a ^7F final state lead to emission of a spin-up electron and vice versa. "Direct (a)" and "resonant (a)1" are processes without spin flips. More complex processes which involve spin-flip transitions are included in the other subdiagrams.

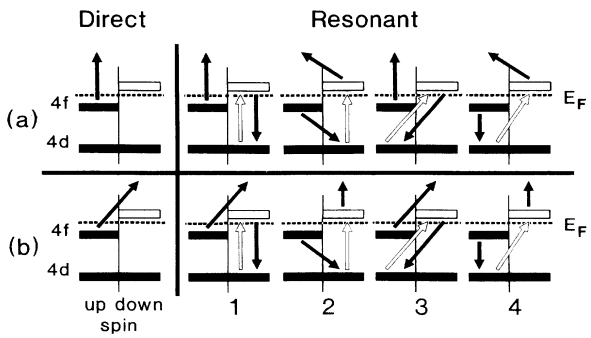

FIG. 1. Schematic picture of the direct and resonant photoemission processes leading to the ^7F final state for RE atoms in $4f^7$ ground-state configuration (see text).

The relative weights of the eight different resonant processes are not known quantitatively but partial information is accessible from an earlier theoretical investigation. Based on the intermediate coupling scheme Sugar has calculated the probability of spin flips in the $4d$-$4f$ photoexcitation for trivalent Gd atoms.[11] For Gd his calculation predicts a weight of about 30% of spin-flip transitions in the primary excitation. This relatively high spin-flip rate is caused by the fact that the resonant excitation involves electrons from the $4d$ subshell of Gd. They show a rather large spin-orbit splitting, comparable to the exchange interaction in the $4f$ subshell. This leads to the invalidity of the LS-coupling scheme. Therefore the spin S is no longer a good quantum number,[8,11,12] i.e., S is no longer to be conserved during photo-excitation. Hence, the processes 3 and 4 in our diagram contribute strongly to the total resonant emission into the ^7F final state. Processes with spin-flip transitions into continuum final states without earlier spin-flip transitions [(b)1 and direct (b)] are presumably of little weight and drawn here only for completeness. The diagram shows that in the intermediate coupling both, spin-conserving and non-spin-conserving processes, should appear independently on the spin multiplicity of the intermediate state (^6X or ^8X). This should reduce the spin polarization of the $4f$ emission in the resonant regime with respect to the direct emission.

Since all processes displayed in Fig. 1 have the same final state they are not distinguishable in spin-integrated photoemission. With the spin-resolved photoemission spectroscopy, we are able to distinguish between emission of a spin-up or a spin-down electron, i.e., spin-conserving [panel (a)] and non-spin-conserving [panel (b)] processes, but still every panel contains four different subdiagrams. The processes (a)1 and (a)2 differ only by a single exchange scattering between the two electrons involved in the deexcitation, therefore both processes are equivalent. The same statement holds for subdiagrams (b)3 and (b)4. Thus, with our experiment we are able to determine the relative weights of spin-conserving and non-spin-conserving two-level processes in the direct and in the resonant regime. Furthermore, assuming the complete spin-conservation in the direct photoemission we can determine the absolute contribution of non-spin-conserving processes to the total resonant emission into

the ^7F final state. We note that non-spin-conservation in the two-level system is not necessarily equivalent to non-spin-conservation in the whole atom since spin-flips of the 5*d* and 6*s* valence electrons are not included in our picture.

III. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum (UHV) chamber for spin and energy resolved photoemission spectroscopy. A 90° spherical capacitor served for energy analysis of the photoelectrons. Their spin polarization was determined by 100-keV Mott scattering. For our experiments the TGM5 wiggler-undulator beamline at the BESSY storage ring[13] provided high intensity linearly polarized vacuum ultraviolet radiation.

Gd was deposited *in situ* by e^--beam evaporation onto the Fe substrate. The base pressure during the photoemission experiments was $(5-7)\times10^{-11}$ mbar. During the Gd evaporation the pressure rose up to $(7-8)\times10^{-10}$ mbar. Our studies were made using two different substrates: an Fe(100) and an Fe(3% Si)(100) picture-frame crystal. Mass equivalences of overlayer thicknesses were calibrated using a quarz microbalance thickness monitor and were found to agree within 10% or better with the results of the earlier photoemission study of this system.[10] The typical evaporation rate was 0.2 ML/min.

The low energy electron diffraction (LEED) pattern of the clean Fe substrate showed sharp (1×1) diffraction spots and became continuously more diffuse with increasing Gd coverage, presumably because of incoherent overlayer growth due to the large bulk lattice mismatch of Fe and Gd. Above coverages of mass equivalences corresponding to two monolayers, LEED spots were no longer detectable.

In our study the substrate was at room temperature during the Gd deposition and during the photoemission experiments. In all cases the photoelectrons were collected in normal emission and at normal incidence of light. The samples were studied in a remanently magnetized state, achieved by applying a short magnetic pulse along a ⟨100⟩ direction of the Fe substrate within the surface plane and parallel to the spin-sensitive direction of the Mott detector. During the measurement no external magnetic field was applied to the sample.

IV. RESULTS

The spin-summed energy distribution curves (EDC's) for increasing Gd overlayer thickness on Fe(100) at $h\nu=70$ eV are presented in Fig. 2. For the direct photoemission the choice of the photon energy is relatively free, but $h\nu=70$ eV corresponds to a high photoionization cross-section of the Gd 4*f* states into continuum states and allows the comparison to the earlier photoemission study. The Fe 3*d* states which are located within about 5 eV below the Fermi level are little affected by the Gd adsorption. A strong feature at 8.2 eV binding energy grows in intensity with increasing overlayer thickness. In accordance with previous investigations we assign this peak to the ^7F final-state configuration of the

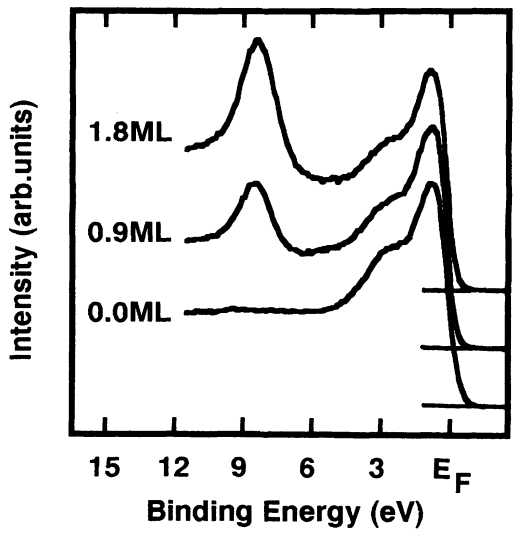

FIG. 2. Spin integrated valence band EDC's of Gd on Fe(100) for increasing coverage at $h\nu=70$ eV.

$4f^6$ multiplet, which is obtained from the trivalent ground state of Gd. The emission of the itinerant 6*s* and 5*d* states is weak and hardly detectable since it overlaps the Fe 3*d* emission.

As one tunes the photon energy through the Gd 4*f* threshold an enormous intensity enhancement of the Gd 4*f* peak is observed. In contrast, the emission of the Fe 3*d* states remains nearly unchanged. In the top panel of Fig. 3 this behavior is shown for 1 ML Gd on Fe(100). As can be seen, the intensity of the *on-resonance* emission at $h\nu=152$ eV (upper curve) of the Gd 4*f* states is by about a factor of 20 larger than the *off-resonance* emission in the Fano minimum at $h\nu=142$ eV (lower curve). The intensity versus photon energy profile is shown in the inset of the figure. The solid line represents the corresponding Fano line shape[14] based on parameters similar to the ones obtained from bulk Gd.[15]

A spin resolved on resonance valence band spectrum of (1 ML Gd)/Fe(100) is displayed in the lower panel of Fig. 3. The sum of spin-up and spin-down intensities is equal to the upper spectrum in the top panel of this figure. It is evident that the Gd 4*f* emission within the giant resonance is highly spin polarized, the intensity mostly appearing in the spin-up channel. One also observes that the spin polarization of the Gd 4*f* states (around 8.2 eV) is of opposite sign than that of the Fe 3*d* states (about 0–5 eV), indicating the ferrimagnetic spin coupling between overlayer and substrate. Therefore, the nomenclature "majority" and "minority" spin is somewhat misleading. Here we define spin-up electrons to be of the same direction as the Gd majority-spin electrons. (Note that the opposite convention has been used in Refs. 9 and 10.)

From Figs. 2 and 3 one can deduce that (1 ML Gd)/Fe(100) is a very fortunate case for the spin-resolved resonant photoemission investigation of a magnetically ordered RE system. First of all, very clean ultrathin layers can be grown under UHV-conditions, as previously

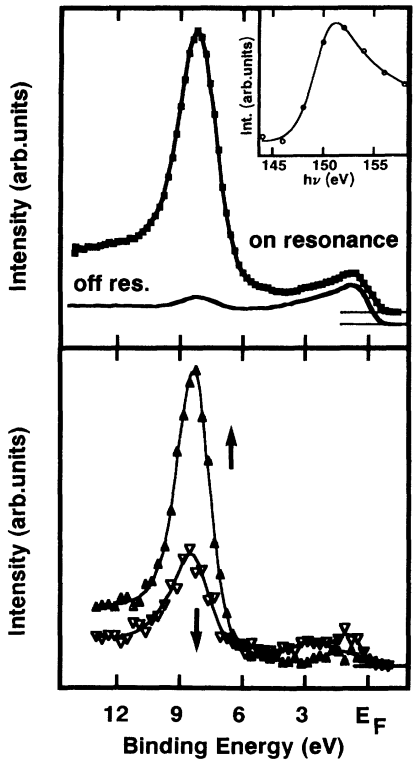

FIG. 3. Top: Spin-integrated valence band EDC's of (1 ML Gd)/Fe(100) at $h\nu=152$ eV (Fano maximum) and at $h\nu=144$ eV (Fano minimum). Inset: $h\nu$ dependence of the Gd $4f$ intensity. The solid line is a Fano profile. Bottom: Spin-resolved on-resonance valence-band spectrum of (1 ML Gd)/Fe(100). ▲: spin-up electrons; ▽: spin-down electrons.

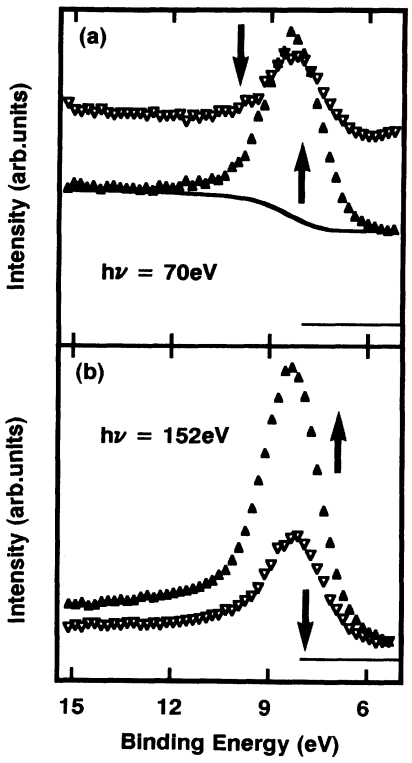

FIG. 4. Spin-resolved EDC's of the Gd $4f$ state for (1 ML Gd)/Fe(100) at $h\nu=70$ eV (top) and $h\nu=152$ eV (bottom). ▲: spin-up electrons; ▽: spin-down electrons. For explanation of the background curve, see text.

shown for Gd (Refs. 8–10) and a number of other RE elements.[16] Second, within its natural linewidth the ^7F final state of the Gd $4f$ emission consists of a single peak. The energy splitting of the J multiplet is too small to be resolved. The peak is located on a flat background of secondary electrons, it is sufficiently separated from the Fe $3d$ states and the signal-to-background ratio is very high. These facts allow a very detailed line-shape analysis. Third, the spin polarization of the Gd $4f$ electrons is quite high. Therefore, it is possible to resolve relatively small changes of the spin polarization as a function of photon energy. And fourth, for Gd the resonant enhancement is extremely large, which makes the interpretation of the resonant character unquestionable.

In Fig. 4 we present spin-resolved EDC's from the Gd $4f$ region only. The spectrum in Fig. 4(a) was taken at $h\nu=70$ eV, the one in Fig. 4(b) at $h\nu=152$ eV. On resonance the peak-to-background ratio is much larger than for the direct photoemission. In the latter the secondary electrons at higher binding energy than the $4f$ peak appear mostly in the spin-up channel, in contrast to the off-resonance spectrum (a). This is simply caused by the high Gd $4f$ to Fe $3d$ intensity ratio.

In the context of this paper the most important measure is the total spin polarization $P_{4f}(h\nu)$ of the electrons emitted from the Gd $4f$ states. It is defined by

$$P_{4f}(h\nu)=\frac{N^{\uparrow}(h\nu)-N^{\downarrow}(h\nu)}{N^{\uparrow}(h\nu)+N^{\downarrow}(h\nu)} ,$$

where $h\nu$ is the photon energy. $N^{\uparrow(\downarrow)}(h\nu)$ is just the $4f$ peak area for spin-up (spin-down) emission above the background. Thus we are left with the problem of determining the background of secondary electrons. Here the difficulty is reduced because we are interested in relative values of peak areas only. The line shapes of spin-up and spin-down peaks appear to be very similar. We have applied a background line shape $B(E)$ which is defined by

$$\left.\frac{dB(E)}{dE}\right|_{E=E_0}=\int_{-\infty}^{E_0} I(E)-B(E)dE .$$

$I(E)$ is the "real" peak intensity function. A typical result is sketched in Fig. 4(a). The output of this procedure is just the two values of the total spin polarizations of the Gd $4f$ peaks

$$P_{4f}(h\nu=70\text{eV})=+(43.3\pm5)\% ,$$

$$P_{4f}(h\nu=152\text{eV})=+(45.7\pm5)\% .$$

We recall that the absolute values of the spin polarization depend on the coverage and the temperature. The incomplete polarization arises, at least to a large extent, from the incomplete alignment of the spin momenta with respect to the spin-sensitive direction of the Mott detector.[9,10] Therefore, we are mainly interested in the com-

parison of the two polarization values on and off resonance.

The experiment has been reproduced several times. Each set of spectra to be compared ($h\nu=70$ and 152 eV) has been taken from the same sample, changing the photon energy only. For this reason thermal and structural conditions were identical and differences in the spin polarization could arise only from differences in the emission processes. Since the accumulation time of a spectrum like those presented in Fig. 4 was of the order of 1 h we have also changed the sequence of collection of direct and resonant photoemission spectra. We have not observed any effect due to aging or contamination under these conditions.

V. DISCUSSION

The main observation in the experiment described above is the equivalence of the spin polarizations in the direct and the giant resonant excitation of Gd $4f$ electrons. Both are found to be identical within the estimated error limits. In Sec. II we have explained why and how non-spin-conserving processes could appear in the resonant excitation and thus lead to a reduced spin polarization of the on-resonance Gd $4f(^7F)$ emission. Our results allow one to exclude the appearance of non-spin-conserving excitations with a weight larger than a few percent.

To our understanding the most important physical quantity to be discussed in this context is the lifetime of the intermediate state and/or the degree of coherence of the excitation and deexcitation transitions. The lifetime of the intermediate states is finite but comparatively very short since the decays are of super Coster-Kronig type. If the resonant emission is understood as real two-step process the intermediate states account for the initial states of the following decay. In the intermediate coupling no conservation law is violated even when the primary optical excitation leads to a ^6X intermediate state. Therefore it is hard to understand why the spin-conserving decay mechanism should be preferential. On the other hand, from our experiment we have clear evidence that the system relaxes to a spin-conserving final state independently on the number of preceding spin-flip transitions.

If the number of ^6X intermediate states is not by far overestimated in Sugar's calculation one has to conclude that the Gd $4f$ emission within the giant resonance is a highly coherent process. In sum the spin flips in electronic transitions involved in the resonant emission process are found to cancel. This also implies that a true two-step picture of the resonant electron emission is hardly applicable.

VI. SUMMARY

With the present work we have show that information about the giant resonance of RE materials can be obtained by spin- and energy-resolved photoelectron spectroscopy. For (1 ML Gd)/Fe(100) the ^7F final state of the Gd $4f$ emission within the giant resonance is strongly spin polarized. Its spin polarization was found to be of the same size as the one in the direct photoemission at $h\nu=70$ eV. These results give direct evidence that, in the case studied, although a number of spin-flip transitions may be involved in the resonant photoexcitation and core hole decay, no enhancement of non-spin-conserving processes takes place in the resonant regime with respect to the direct photoemission. Within the giant resonance the primary excitations and the deexcitations appear to be highly coherent.

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*Present address: BESSY, D-1000 Berlin, Germany.

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