$4f$-$5d$ Resonant Scattering in Spin-Polarized Photoemission

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The spin polarization of the photoelectric current from ferromagnetic gadolinium is expected to decrease monotonically on increasing the photon energy $h\nu$ from threshold to about 10 eV. However, it is found experimentally that a pronounced minimum in the polarization occurs at $h\nu = 6.5$ eV. It is shown that this minimum is due to a quasielastic decay of the optically excited $4f^8$ state into a $5d$ band state.

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Transfer of electrons from $5d$ band states into localized $4f$ states and vice versa is a process well known from studies of intermediate-valence rare-earth materials. It is the purpose of this Letter to show that such a process can also be studied by photoemission. Best suited for this is Gd. It is a ferromagnet and has a localized half-filled $4f$ shell which is in a pure spin state because of dominant s-s coupling within the $4f^n$ configuration. Any additional electron in the $4f^7$ shell must be a down spin and causes the configuration to rise in energy above E_F because of correlation. The $4f^8$ level lies above the vacuum level,[1-4] and it has been suggested that it might produce a large spin dependence in the scattering of low-energy electrons,[5] and other spin-dependent effects.[6] The point of interest here is resonant scattering of hot electrons which consists of absorption of itinerant electrons into quasibound $4f^8$ states and subsequent quasielastic one-electron decay of the $4f^8$ state into band states of the surrounding solid. For an experimental investigation it seems straightforward to use the technique of polarized electron scattering,[7] but the low kinetic energies and high magnetic stray fields make this approach difficult. Similar information can be gained by a photoemission experiment if it is possible to sort out the one-electron decay processes of $4f^8$ quasibound states, since they are inverse to the absorption processes in resonant scattering. This is possible with use of spin-polarized photoemission as shown below. We present direct observation of spin-polarized emission from the decaying $4f^8$ state. This observation implies that strong spin-polarized resonant $4f$-$5d$ scattering does exist in Gd.

Gd films were evaporated *in situ* from a W basket onto a polished Fe pole and checked by Auger analysis at room temperature. Typically twenty cycles of evaporation in pressures below 1×10^{-9} Torr during evaporation were necessary to produce high-quality films with carbon and oxygen impurity levels below 0.1 at.%. The work function of clean polycrystalline Gd was determined by Fowler plots to be 3.2 ± 0.1 eV in agreement with the value of 3.1 ± 0.1 given by Eastman[8] but considerably higher than the one reported in an earlier spin-polarization study.[9] The spin-polarized photoemission technique has been described previously.[10] The polarization measurements were carried out at 220 K, well below the bulk Curie temperature of 298 K. The external magnetic field at the film site was 25 ± 2 kOe. From polarization versus magnetic field data we know that ferromagnetic saturation perpendicular to the film has been achieved.

In Fig. 1 we present the observed integral spin polarization versus photon energy for clean Gd films. The data are accumulated from three different films. The polarization is $P = +25\%$ near photothreshold and decreases with increasing photon energy. It shows a pronounced minimum around 6.5 eV and reaches a roughly constant val-

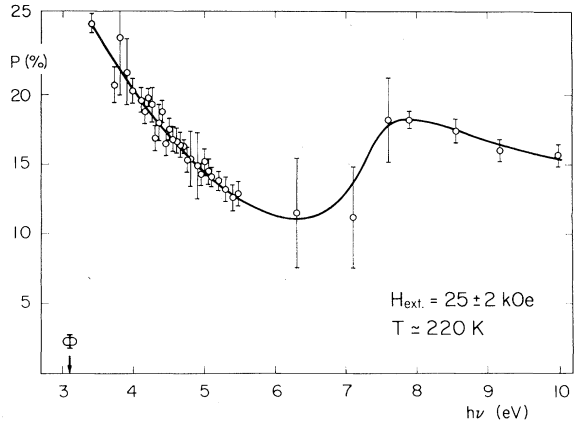

FIG. 1. Spin polarization vs photon energy of photoelectrons from magnetically ordered polycrystalline gadolinium.

ue of $P \simeq 17\%$ at photon energies above 8 eV.[11] The positive (i.e., majority spin predominant) polarization is due to the polarization of the $5d$ electrons in Gd. The minimum shows the emission of photoelectrons from a $4f^8$ photoexcited state as proven below.

In order to interprete the observed spectrum we proceed in two steps: First, we do *not* consider the empty $4f^8$ level. In this case the observed spin polarization from a polycrystalline sample to a good approximation reflects the difference between spin-up and spin-down *initial* densities of states (DOS) of $5d$ electrons. We estimate the polarization by integrating over spin-up and spin-down densities of occupied states. The current carried by spin-up electrons is given by

$$j^{\uparrow}(h\nu) = \text{const} \times \int_{E_F+\varphi-h\nu}^{E_F} N^{\uparrow}(E)\left[1-\left(\frac{E_F+\varphi}{E+h\nu}\right)^{1/2}\right]dE.$$

The term in square brackets is a transmission function or escape cone which restricts emission to electrons with sufficient normal kinetic energy for escape into vacuum. For the DOS $N^{\uparrow}$ and $N^{\downarrow}$ we used ferromagnetic calculations by Harmon and Freeman[12,13] and we obtain $P_0 = (j^{\uparrow} - j^{\downarrow})/(j^{\uparrow} + j^{\downarrow})$ as shown in Fig. 2.[14] The essential features are that all the structure in the $5d$ DOS is removed and that for photon energies higher than 5.5 eV the spectrum is constant, revealing the total magnetic moment of the $5d$-$6s$ conduction electrons. It is evident that the feature at about 7 eV in the observed spectrum cannot be described even with a more realistic final-state DOS without consideration of the empty $4f^8$ level.

As a second step we now take into account the $4f^8$ state. This state is a multiplet of seven narrow lines with a maximum DOS at 4.3 eV above E_F and a total width of ~ 1 eV as observed by bremsstrahlung isochromat spectroscopy (BIS).[1] The itinerant electron states in the corresponding energy range are predominantly $5d$. The d band extends 10 eV above E_F, as observed in Lu with BIS, and has a broad maximum at ~ 5 eV above E_F in Gd.[1] In the qualitative discussion below we therefore will only consider the $4f^8$ and $5d$ states and ignore the $6s$ conduction band.

The localized $4f^8$ level above vacuum level influences spin-polarized photoemission in the following way: A minority conduction electron is photoexcited into the $4f^8$ state. Subsequently this state decays into an itinerant state, and the electron can be emitted. The degree of polarization of this emission depends on the mechanism by which the $4f^8$ state decays. If it decays by Coulomb interaction then it interacts with excitations of both a spin-up and a spin-down electron since the Auger matrix element $\langle d_{v\downarrow}, d_{c\sigma}|V_{\text{Coulomb}}|f_{\downarrow}, d_{v\sigma}\rangle$ is the same for both values of the spin σ if the exchange term is neglected. In this case the spin polarization corresponds to the polarization of the occupied $5d$ states. This two-electron decay would produce extra intensity but would not alter the spin-polarization spectrum P_0. In particular it does not account for the observed minimum at 6.5 eV. Configurational interactions can also be ignored. They are wiped out by the folding of the ~ 1 eV wide ^7F_J multiplet with the occupied width of the d band of ~ 2.5 eV. On the other hand, if the decay of the $4f^8$ state is by a one-electron process, such as f-d hybridization or phonon scattering with quasielastic f-d transition, the minority polarization would be maintained. It is, however, less than -100% since the f^7 final state can be left behind with $S_z = \frac{5}{2}$ which corresponds to a spin-wave emission. For $S = 3$ the reduction is $\frac{3}{4}$ based on spin coupling between the escaping electron and the ion core left behind.[15] The spectral distribution of this current $\Delta j^{\downarrow}(h\nu)$ can be ap-

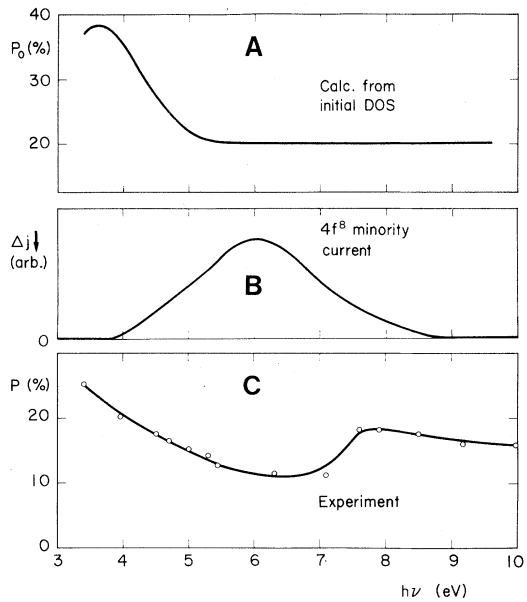

FIG. 2. (a) Calculated spin polarization of the photoelectric current using ferromagnetic initial $5d$-$6s$ DOS of gadolinium (Refs. 12–14). (b) Calculated spectral distribution of the minority current emitted from the decay of the photoexcited $4f^8$ state. (c) Experimental spectrum as in Fig. 1.

proximated by folding the initial minority DOS with the $4f^8$ DOS and a transmission function in the integration. Figure 2(b) shows $\Delta j^{\downarrow}(h\nu)$ calculated by using the same initial DOS as for P_0 and the $4f^8$ DOS as observed with BIS.[1] It is evident from Fig. 2 where the maximum of $\Delta j^{\downarrow}$ lines up with the minimum in the observed spectrum that this minimum can be interpreted as due to one-electron emission from $4f^8$ photoexcited states. From the present data we estimate the relative magnitude α of the current in this channel compared to the direct photoemission current, i.e., $\alpha = \Delta j^{\downarrow}/(j^{\uparrow} + j^{\downarrow})$. For $\alpha \ll 1$ it is $P_{\text{tot}} \simeq P_0 + \alpha P_1$, where $P_1 = -0.75$ is the polarization of the current $\Delta j^{\downarrow}$. We find $\alpha = (8 \pm 3)\%$ at $h\nu = 6$ eV, i.e., the $4f^8$ emission carries $\sim 8\%$ of the total photoelectric current at a photon energy of 6 eV. In order to proceed to a quantitative discussion one has to consider the various strengths of the optical excitations $5d \rightarrow 4f$ and $5d \rightarrow 5d$ as well as of the two one-electron decay mechanisms of the $4f^8$ state mentioned above.

At present little data are available about the strength of the optical transition $4f^7(5d6s)^3 \rightarrow 4f^8(5d6s)^2$ in rare-earth metals in the uv range. From photoemission we know that $4f$-$5d$ excitations are weak.[16,17] $d \rightarrow f$ transitions are expected to be stronger in going from l to $l+1$.[18] However, magneto-optical[4] as well as optical absorption[19] data did reveal rather weak $5d \rightarrow 4f$ absorption. It seems likely that this transition is not strong compared to the $5d$ intraband excitations which give rise to the major fraction of the observed photoemission below 10 eV. This implies that the decay probability of the quasibound $4f^8$ state into an emitting band state must be very high to account for the large minority current observed in this channel.

In Gd the $4f$-$5d$ hybridization in the ground state $4f^7$ configuration is very weak.[20] In the excited $4f^8$ state, however, which is raised by an effective correlation energy of 11.5 eV,[1] the hybridization might be considerably stronger than in the ground state.[20] At this point we cannot be quantitative as to whether this hybridization is strong enough to allow for the observed decay of the $4f^8$ into an itinerant d state. As an alternative process phonon scattering should be considered. In metallic rare-earth chalcogenides ionic radii of the rare earth differ as much as 10% for different valences. As a consequence, many mixed-valent compounds exhibit strong phonon anomalies.[21] The $4f^8(5d6s)^2$ configuration of Gd is like a divalent state and has a considerably larger ionic radius than the trivalent ground state. Excitation and decay of this state therefore are expected to couple to phonons.

We have reported here a direct observation of a strong quasielastic one-electron transition from a $4f^8$ state into conduction states which lead to emission into vacuum. This transition is inverse to the absorption of electrons impinging on the surface into a quasibound $4f^8$ state, i.e., it is equivalent to the absorption and decay processes of resonant scattering. We therefore report that $4f$-$5d$ resonant scattering in Gd does exist and is strongly spin dependent. This is the basis of a new type of spin analyzer as suggested in Ref. 5 which relies on a strongly enhanced absorption of minority electrons due to incoherent resonant scattering. More generally it makes Gd an interesting candidate for further investigations using spin-resolving spectroscopies to gain new information on valence transitions in rare-earth systems.

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[1]J. K. Lang, Y. Baer, and P. A. Cox, J. Phys. F 11, 121 (1981).

[2]J. F. Herbst, R. E. Watson, and J. W. Wilkins, Phys. Rev. B 17, 3089 (1978).

[3]B. Johansson, Phys. Rev. B 20, 1315 (1979).

[4]J. L. Erskine and E. A. Stern, Phys. Rev. B 8, 1239 (1973).

[5]Y. Baer and R. Monnier, Bull. Am. Phys. Soc. 25, 237 (1980).

[6]P. M. Platzman and M. Campagna, Solid State Commun. 36, 449 (1980).

[7]R. J. Celotta, D. T. Pierce, G. C. Wang, S. D. Bader, and G. P. Felcher, Phys. Rev. Lett. 43, 728 (1979).

[8]D. E. Eastman, Phys. Rev. B 2, 1 (1970).

[9]G. Busch, M. Campagna, P. Cotti, and H. C. Siegmann, Phys. Rev. Lett. 22, 597 (1969).

[10]S. F. Alvarado, W. Eib, F. Meier, H. C. Siegmann, and P. Zürcher, in *Photoemission and the Electronic Properties of Surfaces*, edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, New York, 1978), p. 437.

[11]In the earlier study of spin-polarized photoemission from Gd (Ref. 9) much lower polarization values have been observed on films which were evaporated onto cooled substrates. This might indicate that the $5d$-band

contribution to the magnetic moment is reduced in an amorphous sample.

[12]B. N. Harmon and A. J. Freeman, Phys. Rev. B 10, 1979 (1974).

[13]B. N. Harmon, J. Phys. (Paris), Colloq. 40, C5-65 (1979).

[14]The occupied part of the valence band extends over 2 – 3 eV (Ref. 1). This agrees with the value obtained in the relativistic calculation (Ref. 13) but is about twice the one given in Ref. 12. Since in Ref. 13 no minority DOS is presented we used the DOS from Ref. 12. We have corrected the band width simply by scaling the binding energy by a factor of 2.2. This approach is justified since structures in the DOS turn out to be removed by the integration with the given transmission function.

[15]S. F. Alvarado and P. S. Bagus, Phys. Lett. 67A, 397 (1978).

[16]G. Brodén, S. B. M. Hagström, and C. Norris, Phys. Kondens. Mater. 15, 327 (1973).

[17]A. J. Blodgett, Jr., W. E. Spicer, and A. Y.-C. Yu, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland, Amsterdam, 1966), p. 246.

[18]U. Fano and J. W. Cooper, Rev. Mod. Phys. 40, 441 (1968).

[19]H. P. Myers, J. Phys. F 6, 141 (1976).

[20]A. J. Freeman, private communication.

[21]H. A. Mook, R. M. Nicklow, T. Penney, F. Holtzberg, and M. W. Shafer, Phys. Rev. B 18, 2925 (1978).

Velocity Dependence of the Ionization Probability of Sputtered Atoms

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The velocity dependence of the ionization probability of sputtered O^- from chemisorbed oxygen layers on V and Nb is studied. The ionization probability is found to depend on the normal component of the emission velocity, which suggests that the ionization process is an ion-surface interaction and not an ion-atom binary interaction. For $v_\perp > 1\times 10^6$ cm/sec, the ionization probability shows an exponential dependence on $v_\perp$. However, this velocity dependence fails at lower velocities.

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By considering the time-varying potential experienced by the sputtered particle leaving the surface as the origin of the excitation, Blaise and Nourtier[1] and, independently, Nørskov and Lundquist[2] calculated the ionization probability P of secondary ions emitted during sputtering. They both arrived at a similar exponential dependence of P on the component $v_\perp$ of the emission velocity v normal to the surface. According to Ref. 2, P is directly related to the ionization potential I, electron affinity A of the secondary ion, and the work function φ of the substrate surface:

$$P \propto \exp[-(I-\varphi)/\epsilon_0] \text{ or } \exp[-(\varphi - A)/\epsilon_0] \quad (1)$$

for positive and negative ions, respectively. Here the parameter ϵ_0 is velocity dependent. In fact,

$$\epsilon_0 = \hbar\gamma v_\perp / C_1 \pi, \quad (2)$$

where γ and C_1 are defined in Eq. (12) of Ref. 2 and are related to the electronic configurations of the secondary-ion–substrate combination. The exponential dependence of P on φ was observed for the emission of negative secondary ions.[3] However, the $v_\perp$ dependence of P through the parameter ϵ_0 is still under dispute. Published experimental data[4,5] seem to show a certain consistency with an exponential dependence on the emission velocity v. However, in these experiments, the conclusions are based on a comparison of the ion energy distributions (IED) of the secondary ions with the energy distributions of the sputtered neutral atoms which were taken from theory[4] or measured with great difficulty.[5] In addition, so far there has been no reported experiment to demonstrate that both v and the emission angle θ are pertinent in determining the magnitude of the ionization probability. This test is crucial to establish the ionization process as an ion-surface interaction. Recently, Šroubek, Žďánský, and Zavadil[6] argued against such a velocity dependence. They used a computer simulation of the whole sputtering process for a small (six-atom) atomic cluster to show that P for positive secondary ions is quite independent of the

