Spin-polarized Auger electron spectroscopy on Gd

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The spin polarization of all prominent Auger lines of Gd is investigated experimentally. High spin polarization signals are found due to the fully polarized $4f$ shell. In the low energetic Auger lines initiating from a $4d$ hole normal and resonant excitations are identified. In particular, the resonant core hole only transition $N_{45}N_{67}N_{67}$ splits in multiplets where the spin polarization gives evidence of spin-flip processes. A reduced polarization of Auger lines involving $3d$ holes indicates the shortcoming of the LS coupling scheme. We point out that the Gd Auger spin polarization is a key for monitoring this breakdown of spin conservation.

I. INTRODUCTION

Up to now, spin-polarized Auger electron spectroscopy (SPAES) has concentrated on $3d$ transition-metal ferromagnets exclusively.[1] Model systems like single-crystalline Fe and Ni have been investigated to understand the physics behind the measured spin polarization. It has been seen that quite diverse mechanisms lead to the highly structured spin polarization spectra. Core hole only transitions reflect exchange couplings between partly filled shells, normal and resonant Auger processes reveal different excitations, correlation and screening, and transitions involving valence electrons directly monitor the local magnetization through the band polarization.

The availability of local magnetization is, from the point of view of applications, a great promise. The real power of this method lies in its qualitative nature: Often, we do not need a detailed knowledge of the involved Auger process to draw direct conclusions from the experiments on composite systems.[2] This present state of the art, however, will have to be refined, as soon as more complicated systems are investigated. Therefore, a deeper understanding of the underlying physics of the Auger spin polarization is essential. There are mainly two ways to achieve this aim. From the theoretical part, more realistic models should be developed to incorporate valence-band transitions (and hence screening and correlation effects). While this approach seems to be quite hard,[3,4] the experimental contribution to a more fundamental understanding of SPAES is straightforward.

In $3d$ metals like Fe or Ni, spin-orbit interaction is relatively small, and hence spin S and its z component S_z are taken as good quantum numbers. For rare-earth elements, spin-orbit coupling increases appreciably, and S_z no longer is conserved. For certain Auger decays the LS coupling scheme even needs to be replaced by jj coupling, and conservation of S is not guaranteed any more. By SPAES we are able to probe the fundamental limitations of the different coupling schemes, and we show that the spin polarization is still very useful—even if S and S_z no longer are conserved. The test-case element is Gd, which is ferromagnetic below room temperature ($T_C=293$ K), and has a half-filled, highly localized $4f$ shell with $S=\frac{7}{2}$ in the ground state.

We performed spin polarization measurements on all prominent Auger lines of polycrystalline Gd. As expected from the high $4f$ spin, we see large polarization effects on various lines. In particular, core hole only transitions involving $4f$ electrons are polarized intrinsically through the only partially filled $4f$ shell with its large magnetic moment. Furthermore, we easily identify the high spin polarization of resonant Auger processes because of their large energy separation from the normal decay. Finally, the comparison between corresponding $3d$ and $4d$ initial hole Auger processes, $M_5N_{67}N_{67}$ and $N_{45}N_{67}N_{67}$, respectively, will show the beginning of the breakdown of the Russell-Saunders coupling scheme[5] for high-Z materials.

II. EXPERIMENTAL PROCEDURE

The experimental setup used in this work has been described earlier.[6] As a summary, we briefly mention a few essential points. The sample, magnetized parallel to the surface, is irradiated with unpolarized electrons of variable kinetic energy E_p between 250 and 2900 eV. The angle of incidence θ is 70° off surface normal. The secondary electrons emitted from the sample are collected at normal emission with an angular acceptance of $\pm 2.5°$, and energy analyzed by means of a cylindrical mirror analyzer with a resolution of $\Delta E/E=1.1\%$. From the exit aperture of the analyzer the electrons are fed into a Mott detector for spin analysis.

All experiments have been performed on polycrystalline Gd films on top of an Fe(100) single crystal. Films of various thickness (2—30 Å) have been produced by slow evaporation from a tungsten filament, with a rate of 0.5 to 1 Å per minute. The thickness has been determined from comparison of Fe and Gd Auger signals, and is reliable within $\simeq 50\%$. No contaminants could be detected in our Auger system.

The Gd films have been magnetized by the underlying magnetic Fe crystal. Our SPAES measurements show that the Gd magnetic moment is antiparallel to the Fe moment irrespective of the film thickness. This means that a strong antiferromagnetic coupling between the Fe

$3d$ and the Gd $5d$ spins at the interface is present, which is responsible for orientating the $5d$ (and hence $4f$) moments in Gd antiparallel to the externally applied field. This antiferromagnetic coupling between Fe and the Gd overlayer is a fascinating theme in itself and is discussed in detail in Ref. 7. In contrast to Ref. 7, however, in this paper a positive sign of spin polarization P refers to the magnetization direction of Gd rather than of Fe.

All measurements have been carried out at $T=150$ K, i.e., approximately at $T_C/2$. In this regime thermodynamics comes into play for the ferromagnetic coupling between the Gd moments. The zero-temperature case is simulated by looking at thin films of approximately one monolayer thickness, $d\simeq 2$ Å, but again at $T=T_C/2$. We then see enhanced polarization effects compared to thick films with $d\simeq 30$ Å, because the Gd moments are aligned by the strong interaction with the Fe spins in the neighboring substrate layer. By this method, we estimate the polarization in thick Gd films at $T\simeq T_C/2$ to be reduced to $\frac{3}{5}$ of the ground-state value. This does not affect the qualitative discussion presented below, but it should be kept in mind if more elaborate models for the spin polarization of the Auger electrons are considered.

For the moment, the determination of the effective Auger spin polarizations is not at all trivial in Gd. The Auger decays only produce small structures superimposed on the secondary electron cascade, both in intensity and spin polarization spectra. In order to obtain the net spin polarization of the Auger electrons from the measured data we eliminate the secondary electrons created by cascade processes and the inelastically rediffused primary electrons by subtracting backgrounds both in intensity I and polarization P. The effective Auger spin polarization then is obtained as $P_{\text{eff}}=P_0+(P-P_0)I/(I-I_0)$, where P_0 and I_0 are the respective backgrounds. The subtraction of a smooth intensity background is straightforward. The polarization background, however, is strongly energy dependent through depolarization of true secondary electrons from Fe in the Gd overlayer.[7] Therefore, the effective spin polarizations of the Gd Auger lines are accurate only within $\simeq 15\%$.

III. $4d$ CORE HOLE TRANSITIONS

The investigation of the *MMM* Auger decays in the $3d$ transition metals has led to the discovery of strongly polarized resonant features.[1,8] These processes differ from the normal Auger decays in the creation mechanism of the initial hole:

$$3p^6 3d^n \rightarrow 3p^5 3d^n + \epsilon l \quad \text{(normal)},$$

$$3p^6 3d^n \rightarrow 3p^5 3d^{n+1} \quad \text{(resonant)}.$$

Subsequent Auger emission then gives rise to large polarization on the resonant lines, although the intensity is relatively small. The analog to this process in the rare-earth elements is the $4d\rightarrow 4f$ resonant excitation. Here, the atomic picture adopted to describe the transition metals is even more appropriate, because of the highly localized nature of the $4f$ state. Moreover, the energy separation from the corresponding normal Auger decay is large and

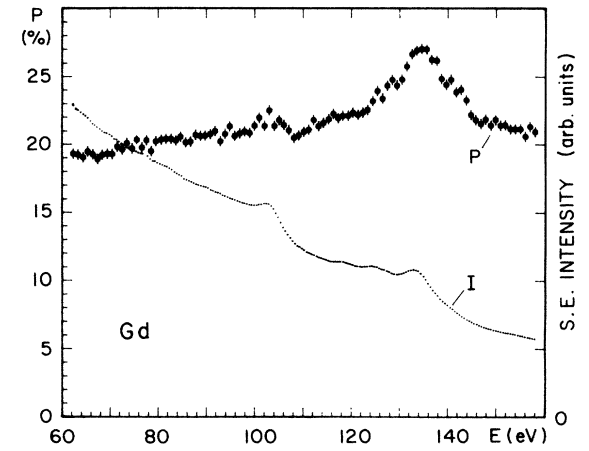

FIG. 1. Spin polarization P and intensity I versus kinetic energy of secondary electrons from a polycrystalline Gd film, excited with primary electrons of 2500 eV; $T=150$ K.

the intensity of the resonant process is quite strong. This clearly helps to identify the resonant process and even allows to investigate the primary energy dependence of its spin polarization.

In Fig. 1, we present spin polarization and intensity spectra versus secondary electron energy in the vicinity of the Gd Auger lines involving the initial $4d$ hole, taken with a primary energy of 2500 eV. The spectra after background subtraction are shown in Fig. 2. The identification of all lines is due to Rivière *et al.*,[9] who improved earlier interpretations.[10]

Both structures at the high-energy end of the intensity spectrum are attributed mainly to resonant excitation $4d\rightarrow 4f$ followed by a super Coster-Kronig decay $N_{45}N_{67}N_{67}$. In the simplest picture these processes are fully polarized, because the emitted $4f$ electron comes from a fully polarized shell. However, spin is not strictly conserved, and spin-orbit coupling gives rise to spin-

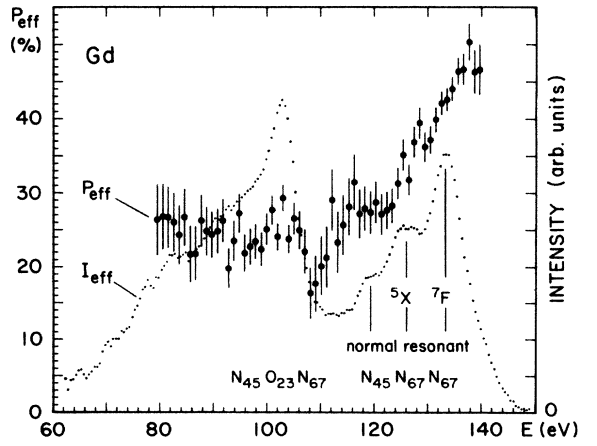

FIG. 2. Effective Auger spin polarization P_{eff} and intensity I_{eff} of Gd, after subtraction of backgrounds in the raw data of Fig. 1.

flipping resonant excitations, although with reduced probability:[11]

$$4d^{10}4f^{7}(^{8}S_{7/2}) \rightarrow 4d^{9}4f^{8}(^{8}X_J) ,$$

$$\rightarrow 4d^{9}4f^{8}(^{6}X_J) \text{ (spin flip)} .$$

Here X_J stands for all possible multiplets conserving total momentum J. The spin-flip process then leads to antiparallel spins of the $4d$ hole and the excited $4f$ electron, which reduces the expected full polarization of the emitted $4f$ Auger electron. But even if the resonant excitation goes to the octet state, two decay channels are open.[12] The spin conserving decay leads to a $^{7}F_J$ state visible with large intensity at 133 eV, whereas the spin-flip process ends up in a $^{5}X_J$, identifiable as a shoulder at 126 eV. The effective spin polarization of these two processes is expected to be large, but smaller for the $^{5}X_J$ state than for the $^{7}F_J$. This is indeed observed experimentally. The effective polarizations, however, are lowered by admixture of weakly polarized transitions at roughly the same energies. The competing nonresonant transitions $N_{45}N_{67}V$ and $N_{45}VV$ should, in close analogy to the $M_{23}VV$ decay in $3d$ transition metals, reflect the density of states and spin polarization of the Gd $5d$ bands.

The large intensity structure at 103 eV is attributed to $N_{45}O_{23}N_{67}$ Coster-Kronig decays. This line is of special interest from a theoretical point of view. As a core hole only transition, it is ideally suited to test models based on molecular orbital calculations[4] or parametrized exchange interactions.[3] We note that the model used for the $3d$ transition-metal $L_3M_{23}M_{23}$ line is not directly transferable. In the case of Gd, one of the involved localized shells is fully polarized in the ground state. This clearly will enhance the polarization over the values expected for exchange coupling to originally full shells with $S=0$, as is the case in transition metals.

The spin polarization of the small intensity structure at 120 eV is an unsolved riddle. Rivière *et al.*[9] ascribe this shoulder to normal $N_{45}N_{67}N_{67}$ Auger decays. We expect spin polarization as high as on the resonant line at 133 eV, even if again spin conservation may partly be relaxed. This is in contrast to the experiment: $P_{\text{eff}} \simeq 28\%$ for the normal $N_{45}N_{67}N_{67}$ decay is substantially lower than $P_{\text{eff}} \simeq 42\%$ for the corresponding resonant decay at 133 eV, and the discrepancy is clearly out of statistic or systematic errors. We note that the high energetic analog with the same final state, the $M_5N_{67}N_{67}$ line at 1168 eV, has even lower polarization, $P_{\text{eff}} \simeq 18\%$, see Table I. At present, we are not able to explain the difference in polarization between the normal and the resonant $N_{45}N_{67}N_{67}$ Auger line. We believe, however, that due to the clear separation of normal and resonant line, the observed polarization discrepancy gives further impetus to a deeper understanding of different deexcitation mechanisms.

Furthermore, we were able to detect a primary energy dependence of the effective polarizations of resonant and normal Auger processes, see Table I. If we reduce the primary energy E_p to near threshold ($E_{4d}=143$ eV (Ref. 13)], the polarizations on the resonant lines decrease, whereas P_{eff} on the normal lines remains essentially constant. Near threshold, there are two competing effects which partly cancel. First, the resonant $4d \rightarrow 4f$ excitation can also lead to $4d_{\uparrow}$ holes because of exchange scattering of the promoted $4d_{\uparrow}$ electron with a down-spin primary electron, preferably at low primary energy. Then, the spin polarization of the emitted Auger electron is reduced although no spin-flip process is involved. Second, we expect the ratio of resonant to nonresonant decay to increase at low primary energy by phase space arguments. The Auger lines at 126 and 133 eV, consisting of a mixture of both resonant and normal parts, should then show a higher polarization.

The experimental result of a lower spin polarization at low primary energies obviously shows that for resonant $4d \rightarrow 4f$ excitations the first process is much more efficient for $E_p \leq 2E_{4d}$. Analogous behavior for $3d$ transition metals is expected for $3p \rightarrow 3d$ excitations.

TABLE I. Effective Auger spin polarizations (in %) of all prominent lines in polycrystalline Gd calculated as described in text. The errors are $\leq 15\%$ of the given values. Apart from the thick film ($d=30$ Å) described in this work, the values for a thin film are given for comparison. Note the primary energy dependence of the resonant lines.

Transitions \ Primary energy	2500 eV ($d=2.4$ Å)	2900 eV ($d=30$ Å)	2500 eV ($d=30$ Å)	500 eV ($d=30$ Å)	250 eV ($d=30$ Å)
$N_{45}O_{23}N_{67}$	33		24	21	18
$N_{45}N_{67}N_{67}$	42		28	24	25
$N_{45}N_{67}N_{67}$ res. (^{5}X) $N_{45}N_{67}V$	59		31	27	20
$N_{45}N_{67}N_{67}$ res. (^{7}F) $N_{45}VV$	77		42	42	29
$M_5N_{45}N_{45}$ ($S=0$)		18			
($S=1$)		-6			
$M_4N_{45}N_{45}$ ($S=0$)		10			
($S=1$)		-5			
$M_5N_{45}N_{67}$		20			
$M_5N_{67}N_{67}$		18			

IV. 3d CORE HOLE TRANSITIONS

One point is of particular interest in the Gd Auger transitions with an initial $3d$ hole. While $4d^9 4f^n$ states are thought to be still described reasonably in the LS coupling scheme,[14] jj coupling is more appropriate for $3d^9 4f^n$ states.[9,15] The spin polarization of the $M_{45}NN$ Auger transitions then reflects the onset of breakdown of total spin S as a good quantum number.

In Fig. 3, we present the Gd Auger features originating from the decay of $3d$ holes, excited with a primary energy of 2900 eV. We note that none of the three prominent lines involves valence electrons. Hence the spectrum offers a new challenge to theorists describing core hole only transitions in a quasiatomic approach.[3] In contrast to the LMM lines of Fe or Ni with a single core hole only transition, here the whole spectrum ought to be consistently described with one set of fit parameters for all lines.

The breakdown of the LS coupling scheme is illustrated nicely by the Auger line at 1168 eV, $M_5N_{67}N_{67}$. The final state is identical to the low energy $N_{45}N_{67}N_{67}$ decay at 120 eV. The effective spin polarizations, however, are markedly different, see Table I. The $M_5N_{67}N_{67}$ transition with $P_{\text{eff}} \simeq 18\%$ is substantially less polarized than the $N_{45}N_{67}N_{67}$ line, where $P_{\text{eff}} \simeq 28\%$. This indicates that spin conservation in the presence of the deep $3d$ core hole no longer holds. Qualitatively, the spin-orbit interaction has increased appreciably relative to the exchange splitting, and jj coupling is more appropriate now. For the moment, we cannot draw conclusions beyond this, because no multiplet calculations are available, neither in jj, nor in the (admittedly less suited) LS coupling scheme.[16]

The breakdown of spin conservation further is manifest by the fact that the effective polarization on the $M_5N_{45}N_{67}$ line, $P_{\text{eff}} \simeq 20\%$, is approximately equal to the one on the $M_5N_{67}N_{67}$ peak. If spin were a good quantum number, we certainly would expect higher polarization on the $M_5N_{67}N_{67}$ line just by the fact that the N_{45} electrons can have both spins with almost equal probability.

At $E \simeq 880$ eV, $M_5N_{45}N_{45}$ decays give rise to the largest intensity structure with initial $3d$ hole. The effective spin polarization is 18% at $E \simeq 870$ eV, gradually decreasing to -6% at $E \simeq 890$ eV. The resemblence to the $L_3M_{23}M_{23}$ Auger line in Fe or Ni is astonishing. There, the spectral behavior reflects the singlet-triplet splitting of the two final-state holes. If the shortcomings of the LS coupling scheme are neglected for a moment, we can adapt the concepts developed for the $L_3M_{23}M_{23}$ line in $3d$ transition metals. The exchange splitting between singlet and triplet state obviously survives to a good amount. Again we expect the positively polarized Auger electron from the singlet state to have lower kinetic energy than the one from the triplet state as a consequence of the general trend that the atomic ground states are high spin states.[17] Keeping this in mind we then expect a spectral behavior quite analogous to the $L_3M_{23}M_{23}$ line in Fe or Ni, with enhanced polarization effects because of the additional coupling to the fully polarized $4f$ shell, and this is exactly what is observed experimentally.

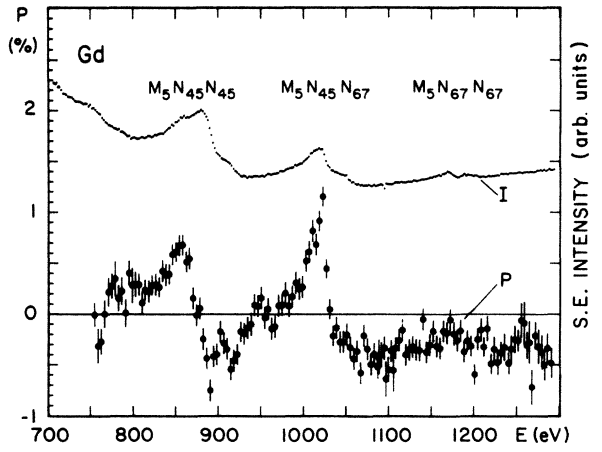

FIG. 3. Spin polarization P and intensity I versus kinetic energy of secondary electrons from a polycrystalline Gd film, excited with primary electrons of 2900 eV; $T = 150$ K. The background polarization is slightly negative because of inversely polarized electrons emitted from the Fe substrate.

The high-energy shoulder in intensity at $\simeq 910$ eV is attributed to $M_4N_{45}N_{45}$ decays. The same reasoning must be true for both $3d$ initial holes, whether $J = \frac{3}{2}$ or $J = \frac{5}{2}$, if jj coupling is not too important. The discrepancy between the singlet state polarizations $P_{\text{eff}} \simeq 10\%$ and $P_{\text{eff}} \simeq 18\%$ for M_4 and M_5 excitations, respectively, is most likely due to a partial coincidence of M_5 ($S = 1$) and M_4 ($S = 0$) decays.

V. CONCLUSIONS

The present understanding of the Auger spin polarization in Gd is at best qualitative, and mainly based on arguments using analogies to the $3d$ transition metals. This approach has proven useful for the low energetic Auger transitions. The large spin polarization on the various lines is reasonably interpretable within the concept of LS coupling in terms of normal and resonant Auger processes. Particular interest has been given to the $N_{45}N_{67}N_{67}$ decay as an example of a core hole only transition involving a highly polarized shell.

For the high energetic $M_{45}NN$ processes, on the other hand, we see from the measured spin polarization that the LS coupling scheme cannot be justified any longer. More appropriate theories are necessary but not yet available. Hopefully they might be stimulated by this work.

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