Lifetime Widths of Surface States on Magnetic Lanthanide Metals

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Low-temperature scanning tunneling spectroscopy is used to study electronic structure and dynamics of d-like surface states of trivalent lanthanide metals from La to Lu. The magnetic exchange splitting of these states is found to scale with the 4f spin multiplied by an effective exchange-coupling constant that increases with 4f occupancy in an approximately linear way. The dynamics of the surface states, as revealed by the lifetime width, is dominated by electron-phonon scattering in the occupied region and by electron-magnon scattering in the unoccupied region, respectively.

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Electronic structure and dynamics of surface states have recently attracted substantial attention. For the noble metals, a profound understanding of binding energies and lifetimes of surface states has been achieved, mainly due to improvements in the experimental and theoretical techniques [1]. Here, for defect-free surfaces the lifetime of a surface state is predominantly determined by electron-phonon (e-ph) and electron-electron (e-e) scattering rates, with the latter including both intraband and interband excitations [2]. On the other hand, much less is known on surface-state dynamics in transition metals, particularly in the lanthanides. Across the series, the lanthanide metals have similar conduction-band structures but different 4f occupancies, n_{4f}, and hence different 4f-spin moments that interact with the (5d6s)-conduction electrons and the surface state by exchange interaction. Below specific temperatures, all lanthanide metals with non-vanishing 4f moment exhibit long-range magnetic order that causes an exchange splitting of the electronic states. [3, 4, 5, 6]. For these magnetic transition metals, collective excitations of spin waves (magnons) provide additional decay channels for excited electronic states [7]. Electron-magnon (e-m) scattering processes, where an electron undergoes a spin-flip and a magnon is either created or annihilated, are difficult to distinguish from e-ph scattering processes since both are expected to exhibit similar temperature dependences [8].

The electronic structure of surface states and their dynamics can be studied by various techniques including photoemission (PE), inverse photoemission (IPE), two-photon-photoemission (2PPE), and scanning tunneling spectroscopy (STS) [8]. While 2PPE is a time-resolved technique that can directly determine relaxation times, PE, IPE, and STS measure spectral lifetime widths of electronic states, i.e. inverse lifetimes.

In this Letter, we report on a systematic low-temperature STS study of the 5d_{z^2}-like surface states on the (0001) faces of trivalent lanthanide metals. The magnetic exchange splitting, \Delta_{ex}, of these laterally localized surface states is found to scale with the 4f spin moment multiplied by an effective exchange-coupling constant that increases with n_{4f} in an approximately linear way due to lanthanide contraction. Concerning the dynamics of the surface states, we find much shorter lifetimes for the (unoccupied) minority states as compared to the (occupied) majority states. While the lifetimes of the occupied states are mainly determined by e-ph scattering, the lifetimes of the unoccupied states are dominated by e-m scattering.

The experiments were performed in an ultrahigh vacuum (UHV) chamber equipped with a low-temperature scanning tunneling microscope (STM) operated at 10 K. The samples were prepared in-situ by electron-beam evaporation of the lanthanide metals La (4f^0), Nd (4f^3), Gd (4f^7), Tb (4f^8), Dy (4f^9), Ho (4f^{10}), Er (4f^{11}), Tm (4f^{12}), or Lu (4f^{14}), respectively, and deposition on a clean W(110) single crystal kept at room temperature. Subsequently, the samples were annealed at temperatures between 500 and 1000 K, resulting in smooth hcp (0001) films (dhcp in case of La and Nd) with atomically flat terraces, and local-thickness variations of only a few monolayers (ML) [9]. The average thickness of the deposited film was monitored with a quartz microbalance. STS spectra were recorded with fixed tip position and switched-off feedback control. The differential conductivity, dI/dU, with I being the tunneling current and U the sample bias voltage, was measured as a function of U by modulating U and recording the induced modulation of I via lock-in technique. dI/dU is proportional to the density of states at the sample surface in good approximation. A modulation amplitude of 1 mV (rms) at a frequency of \approx 360 Hz was used, with the time constant of the lock-in amplifier set to 100 ms, at a sweep rate of \approx 6 mV/s. To correct for binding energy shifts due to the finite time constant, the spectra were recorded in both directions, from lower to higher and from higher to lower sample bias. Since both the STM tip and the sample were cooled to 10 K, the energy resolution was \approx 3 meV, corresponding to 3.5 kT.

Fig. 1 shows tunneling spectra of the trivalent lanthanide metals La, Nd, Gd, Tb, Dy, Ho, Er, Tm, and Lu. The d-like surface states are clearly resolved as pro-
nounced peaks. For the lanthanides with non-vanishing 4f-spin moments, majority and minority exchange-split spin states appear below and above $E_F$ ($U = 0$), respectively. For La and Lu, with $n_{4f} = 0$ and $n_{4f} = 14$, respectively, the spectra exhibit a single peak. The strongly peaked density of surface states probed by STS is the consequence of a high degree of lateral localization, resulting in small dispersions of the surface-state bands with effective masses $m^*/m \gg 1$. For Nd and Tm, with the majority surface states rather close to $E_F$, and possibly also for Lu, additional sharp features directly at $E_F$ show up in the STS spectra that represent many-body resonances due to an interaction of the localized surface state with bulk conduction electrons; hence, these features can be described by Fano line shapes.

Due to the small dispersions of the surface-state bands, the surface-state peaks in the tunneling spectra can be described by Lorentzian lines, with widths $\Gamma$ that are related to lifetimes $\tau$ by $\Gamma = \hbar/\tau$. Only for narrow peaks, small deviations from a symmetric line shape due to dispersion are recognizable. Since the surface-state bands show a downward dispersion with a band maximum at $\Gamma$ (with the exception of Lu, for which an M-shaped dispersion had been calculated), the trailing edges of the peaks in the STS spectra are generally steeper than the leading edges. In order to account for this asymmetry, the peaks were fitted with adequate superpositions of Lorentzian lines; a detailed description of the fit procedure is given in Ref. 5. Fit results for energies and linewidths in the present work refer to surface states at the band maximum. In case of Nd and Tm, the trailing edges of the surface-state peaks are superimposed on the mentioned resonances at $E_F$, and the asymmetries of the peaks cannot be determined unambiguously. Therefore, single Lorentzian lines were fitted to these peaks. The errors that result from a neglect of surface-state dispersion are less than 10 meV for both the energies and the widths of the surface state.

Table I summarizes the fit results for the energies, $E_{\uparrow}$ and $E_{\downarrow}$, and the widths, $\Gamma_{\uparrow}$ and $\Gamma_{\downarrow}$, of the majority ($\uparrow$) and minority ($\downarrow$) surface states as obtained from numerous STS spectra for each lanthanide metal. The exchange splittings, $\Delta_{ex} = E_{\downarrow} - E_{\uparrow}$, are plotted in Fig. 2(a) versus the 4f-spin quantum number $S$. A systematic deviation from a linear dependence is clearly observed. Furthermore, Nd exhibits a much smaller exchange splitting than Er, although both elements have the same 4f spin.

In the following, we discuss the lifetime widths of surface states. In Fig. 2(b) the $\Gamma$ values, listed in Table II, are plotted versus surface-state energies. As indicated by

![STS spectra of (0001)-surface states of the trivalent lanthanide metals recorded at 10 K. The spectra are overview spectra. Better resolved spectra of each peak were used for data analysis, as described in detail in Ref. 5.](image)
the two shaded areas, the lifetime widths of the majority states below \( E_F \) are considerably smaller than those of the minority states above \( E_F \). In a previous study of Gd and Ho \( \beta \) \cite{5, 14}, the enhanced lifetime widths were attributed to the larger absolute energies, |\( E - E_F \)|, of the unoccupied minority states, which, according to 3-dimensional Fermi-liquid theory, would result in increased e-e scattering rates: \( \Gamma_{\text{e-e}} = 2\beta \cdot (E - E_F)^2 \) \cite{15}. In this way, \( 2\beta \) values between 0.2 and 0.5 eV\(^{-1} \) were obtained, which are, however, up to an order of magnitude larger than the \( 2\beta \) values reported for other materials \cite{1}, including Yb, a divalent lanthanide metal with a 4f\(^{14} \) configuration. In case of Yb, \( 2\beta \approx 0.08 \) eV\(^{-1} \) was recently determined from lifetime widths of quantum-well states in thin Yb(0001) films \cite{16}. Although we cannot completely rule out the possibility of large \( 2\beta \) values, the present results, based on a systematic study of trivalent lanthanide metals, renders the previous conclusion questionable.

For surface states that lie in the center of a bandgap of the projected bandstructure, interband-transition rates are expected to be small since such transitions involve large momentum transfers, \( \Delta k \), and the Coulomb interaction scales with \( \Delta k^{-2} \) \cite{1}. Intra-band transitions, on the other hand, may give significant, in some cases even dominant contributions to lifetime widths \cite{17}. In the tunneling process, holes (\( U < 0 \)) and electrons (\( U > 0 \)) are predominantly excited at \( \Gamma \), i.e. at the maximum of the surface-state band. While an excited electron in an unoccupied surface-state band can decay into lower-lying electronic states of the same band, there are no intra-band decay channels available for a hole in an occupied surface-state band at \( \Gamma \). We therefore conclude that the dominant contribution to lifetime widths of the occupied surface states is e-ph scattering. For Lu, the surface-state energy is smaller than the Debye energy so that even e-ph scattering is suppressed \cite{1}. From temperature-dependent measurements of Gd surface states, the zero-temperature contribution of e-ph scattering to the lifetime width was determined as \( \Gamma_{\text{e-ph}} = (22 \pm 5) \) meV \cite{14}. Thus, e-ph scattering accounts for approximately 70% of the total lifetime width. Similar values can be expected for the other lanthanide metals.

For unoccupied surface states, intraband e-e scattering will be enhanced, explaining the increased lifetime width of the unoccupied La-surface state by about 25 meV as compared to those of the occupied surface states.

So far, we have not taken into account e-m scattering of surface states due to exchange interaction with the 4f spins. For the occupied surface states, the same argument as given above for e-e scattering applies, i.e. the number of states into which an excited hole at or close to the surface-state band maximum can scatter is limited. Furthermore, due to the high degree of spin polarization of the surface state bands, intraband spin-flip scattering is suppressed, even for excited states below the surface-state band maximum. Previous studies of

| \( \Gamma \) (meV) | 49 | 70 | 120 | 33 | 134 | 22 | 184 | 19 | 170 | 19 | 125 | 30 | 146 | 29 | 190 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| \( E - E_F \) (meV) | 130 | -18 | 187 | -191 | 470 | -111 | 474 | -102 | 402 | -90 | 347 | -51 | 318 | -19 | 2 |

**TABLE I:** Lifetime width, \( \Gamma \), and energy, \( E - E_F \), of exchange-split (0001)-surface states on trivalent lanthanide metals. The estimated errors of the energies are ±10 meV, in case of Lu ±1 meV. The errors of the \( \Gamma \) values are plotted in Fig. 3. Majority and minority states are denoted by \( \uparrow \) and \( \downarrow \), respectively.

FIG. 2: (a) Exchange splitting of (0001)-surface states, \( \Delta_{sz} \), at 10 K plotted versus 4f spin, \( S \), of the studied lanthanide metals. (b) Effective exchange-coupling constant, \( J_{	ext{eff}} \), and lattice constant, \( a \), plotted versus 4f occupancy, \( n_{4f} \), of various lanthanide metals.
Gd based on spin-resolved PE found an e-m-scattering contribution of ≈ 14 meV to the lifetime width of the majority-spin state, but only if the state is more than 25 meV – the highest magnon energy – below the band maximum. Due to the small dispersions of the surface-state bands, most excited holes will be closer to the band maximum so that the actual contribution of e-m scattering will be smaller.

For unoccupied surface states on magnetic lanthanide metals, both intraband and interband spin-flip transition rates will be enhanced. This explains the large lifetime widths compared to those of the occupied surface states and also to that of the unoccupied surface state on non-magnetic La metal. Again, intraband spin-flip transitions are only possible if the spin polarization of the surface-state band is less than 100%, e.g., due to spin-orbit coupling. As for interband transitions, it is interesting to note that for Gd, and presumably also for the other magnetic lanthanide metals, the unoccupied minority surface-state band lies outside the bandgap of the projected majority bandstructure, whereas the occupied minority surface states are located within the total, spin-averaged bandgap. Therefore, spin-flip transitions by magnon emission do not require large momentum transfers, as spin-conserved transitions do, which could explain the enhanced scattering rates. If we make the assumption that the differences in lifetime widths of the unoccupied surface states on magnetic lanthanide metals, on the one hand, and the lifetime width of the surface state on La(0001), on the other hand, is solely due to e-m scattering, the e-m contribution amounts to ≈ (100 ± 25) meV; the error bar reflects the scattering of data points for different metals (see Fig. 3).

Finally, we like to mention that the rather large lifetime width of the occupied surface state on Nd is probably also due to e-m scattering. While the exchange-split surface states of the heavy lanthanide metals are nearly 100% spin polarized, the net polarization of Nd surface states vanishes due to the antiferromagnetic spin order within the (0001)-surface plane, allowing for enhanced spin-flip intraband scattering.

In summary, the present work provides detailed information on the electronic structure of surface states on lanthanide metals, in particular on their energies, exchange splitting, and dynamics. At this point, theoretical calculations are needed to corroborate the experimental findings and conclusions regarding the influence of lanthanide contraction on exchange splitting as well as the contribution of e-ph, inter- and intraband e-e, and e-m scattering to the lifetime widths of the surface states.

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FIG. 3: Lifetime width, Γ, versus surface-state energies, E − E_F, for the trivalent lanthanide metals according to measured values listed in Table I.

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