Enhanced Spin Polarization of Conduction Electrons in Ni, explained by comparison with Cu

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The spin–split Fermi level crossings of the conduction band in Ni are mapped out by high–resolution photoemission and compared to the equivalent crossing in Cu. The area of the quasiparticle peak decreases rapidly below Ef in Ni, but not in Cu. Majority spins have larger spectral weight at Ef than minority spins, thereby enhancing the spin–polarization beyond that expected from the density of states. A large part of the effect can be traced to a rapid variation of the matrix element with k at the point where the s,p–band begins to hybridize with the d$^{5}$ state. However, it is quite possible that the intensity drop in Ni is reinforced by a transfer of spectral weight from single–particle to many–electron excitations. The results suggest that the matrix element should be considered for explaining the enhanced spin polarization observed for Ni in spin–polarized tunneling.

I. SPIN–POLARIZED CURRENTS IN MAGNETOELECTRONICS

The rapidly growing field of magnetoelectronics [1–3] is largely based on the manipulation of spin currents that are carried by electrons at the Fermi level $\epsilon_F$. Examples are the application of giant magnetoresistance (GMR) in reading heads for hard disks and the use of spin–polarized tunneling [4,5] and junction magnetoresistance (JMR) for a magnetic random access memory (MRAM). Spin–polarized tunneling is also being explored for high–resolution magnetic imaging by scanning tunneling microscopy (STM) [6,8]. The magnitude of the magnetoresistance increases with the spin polarization of the currents, likewise the magnetic contrast in STM. A variety of efforts are directed towards designing new magnetic materials with higher spin–polarization, such as half–metallic compounds and nanostructures. For making systematic progress one first has to identify the electronic states that are responsible for the spin currents, then determine the fundamental parameters relevant for spin polarization, and eventually apply this knowledge to the design of new magnetic materials.

The character of the spin carriers in ferromagnets has been debated for some time [19,27]. The initial puzzle has been whether s,p– or d–electrons dominate transport properties [21]. The s,p–states have high group velocity, but low density of states and weak magnetism. The d–states carry the magnetic moment and have high density of states, but their group velocity is low. This dilemma can be resolved by looking at a realistic band structure where a free–electron–like s,p–band hybridizes with the magnetic d–levels close to the Fermi level [21]. That allows the s,p–band to acquire a significant magnetic splitting [14,16].

The origin of the spin–polarization in is still under intense investigation [18,19]. Various mechanisms have been proposed, such as a spin dependence of the density of states, spin–dependent electron scattering in the bulk and at interfaces, and a spin–dependent matrix element. A direct determination of the spin polarization from magneto–transport properties is difficult. An extensive set of values has been reported for spin–polarized tunneling into superconductors [15] and Andreev reflection at point contacts to superconductors [15,19]. The traditional explanation of such data has been the imbalance in the density of states at $\epsilon_F$ for a magnetically–split free–electron band [14]. It has been fairly successful for explaining the spin–polarization of Fe, but has failed for Ni where the observed spin–polarization of 23%–46% far exceeds the 6% spin–polarization expected from the density of states [15,19,21]. A variety of more sophisticated approaches have been proposed for explaining spin–polarized tunneling [21,22,23]. It is highly desirable to achieve high spin–polarization in tunneling from Ni alloys, such as permalloy (Ni$_{80}$Fe$_{20}$), since permalloy is the most common material in magnetoelectronics.

It is difficult to pinpoint the parameters relevant for achieving high spin–polarization from transport data alone. Such measurements integrate in k–space over the Fermi surface and involve additional parameters, such as scattering lengths. Angle–resolved photoemission is able to focus onto specific k–points [24] and to separate out scattering lengths [14]. Traditionally, this technique has lacked sufficient energy resol-
tion for discerning the electronic states that are relevant for transport phenomena, that is those within a few thermal energies kT of εf. In our study, the energy resolution is 9 meV for electrons plus photons, compared to kT=25 meV at room temperature. Tunable synchrotron radiation allows us to map out the k component perpendicular to the surface independent of the parallel components. As non–magnetic reference material we use Cu. It has the same crystal structure as the adjacent Ni and a similar band topology. The main difference is an energy shift of the d–bands, which lie 2 eV lower in Cu than in Ni.

Our key observations are two intensity anomalies in the spin–split Ni conduction band: Below εf the band loses intensity very rapidly in Ni but not in Cu. Furthermore, majority spins have larger photoemission intensity at εf than minority spins. That creates an extra spin–polarization beyond the higher density of states for majority spins (which enters when integrating k over the Fermi surface). Several possible explanations are explored, such as increased electron scattering below εf, a photoemission matrix element that varies rapidly with E and k, and a transfer of spectral weight from single–electron excitations to many–electron excitations. Judging from our comparison with Cu and from simple matrix element calculations we assign the anomalies in Ni in large part to a rapid decrease of the matrix element at the point where the s,p–band becomes more d–like. Our finding suggests that a similar role can be expected from the matrix element in other phenomena, such as in spin–polarized tunneling.

II. MANYBODY STATES, SPECTRAL FUNCTION, AND MATRIX ELEMENT

For encompassing the possibility of manybody interactions and electron scattering it is useful to start out with a very general characterization of electronic states in solids. That can be achieved by a spectral function A(k, ω) which describes the spectral weight as a function of energy E = ħω and momentum p = ħk. In a band structure model, where only single–electron excitations are possible, A(k, ω) consists of sharp d–function peaks. The spectral function is far more general than this, however, and can describe all the many–electron effects measurable in a photoemission experiment. This generality is particularly useful for describing correlated electrons in the partially–filled 3d–shells of ferromagnets. Ni exhibits a broad satellite several eV below the single–hole states [21–28] which may be viewed as a pair of correlated d–holes. The consequences of the two–hole satellite for the single–particle excitations in Ni are a reduction of the band width by 40% and a decrease of the magnetic splitting by a factor of 2–3 [24–27]. These discrepancies have been associated with spectral weight shifting from the single–hole d–bands down to the two–hole satellite while preserving the center of gravity of the energy spectrum. A trading of spectral weight between single– and multi–electron excitations has been observed in adsorbates [29] and oxides [30], too.

Such a manybody effect will be considered as one of two plausible explanations for the drop of the photoemission intensity below εf in Ni. The line of thought is the following: The conduction band in Ni is s,p–like above εf but acquires more d–character below εf as it starts hybridizing with the d–bands. The increasing d–character makes it prone to many–electron effects, such as a transfer of spectral weight to the two–hole satellite. Even the smaller intensity of the minority–spin peak at εf would find a natural explanation in such a scenario, because the minority–spin d–bands lie higher in energy and hybridize more with the minority–spin conduction band at εf. For assessing this hypothesis we use Cu as reference material where many–electron effects weak. For example, the intensity of the two–hole satellite is 21% of the one–hole states in Ni, but only 2.5% in Cu [32].

The spectral function A(k, ω) is related to the angle–resolved photoemission intensity I(ω, k) by a matrix element M(k, ω), that is specific to the photoemission process [31]:

\[ I(k, \omega) = A(k, \omega) \times |M(k, \omega)|^2 \times f(\omega) \]  (1)

The Fermi–Dirac function f(w) gives the occupancy. The spectral function itself has the form

\[ A(k, \omega) = -\frac{1}{\pi} \Im \left\{ \frac{1}{\omega - \epsilon_0(k) - \Sigma(k, \omega)} \right\} \]  (2)

containing the complex self–energy Σ(k, ω) and the electron band dispersion ϵ0(k). A fundamental sum rule for the spectral function implies a trade–off between single–electron and many–electron excitations:

\[ \int A(\omega, k) d\omega = 1 \]  (3)

The Fermi–Dirac function is absent, thus requiring an extrapolation of photoemission data above the Fermi level, or the inclusion of inverse photoemission data. One remaining piece in Eq. 1 to be determined is the matrix element M(k) for single–hole excitations from the Σ1 band:

\[ M(k) = \langle Y_{final}(k) | \hat{A}_p | Y_{initial}(k) \rangle \]  (4)

A is the vector potential of the photon and p the momentum operator. We have performed an estimate of M(k) by using a combined interpolation scheme that takes the correct band width and splitting of the Ni d–bands into account [32].

III. THE PHOTOEMISSION EXPERIMENT

In photoemission, the parallel component k∥ is conserved and can be determined directly from the kinetic energy Ekin and the polar angle J of the photoelectrons. The perpendicular component k⊥ varies with the photon energy ħω and can be estimated using a free electron upper band with an inner potential [28–33]. In order to obtain a clear–cut spectral function we designed the experimental geometry such that it isolates a single band crossing the Fermi level with a high photoemission cross section. This is achieved by selecting the Σ1 conduction band along the [110] direction in k–space. It crosses εf about half–way between Γ and X and stays as far from the
d–bands as possible [33]. Dipole selection rules provide additional selectivity: The choice of p–polarized light with the electric field vector in the photoemission plane enhances the \( \Sigma_1 \) band due to its even mirror symmetry and eliminates d–bands with odd symmetry. As a result, the photoemission data in Fig. 1 clearly show a single conduction band for Cu and a spin–split version of that band for Ni.

As a consistency check we map the same Fermi level crossing from two different surfaces, the (100) and the (110). For the (100) surface we reach the desired location [33] with a photon energy \( h\nu=44 \) eV for Ni (\( h\nu=50 \) eV for Cu), combined with a polar angle of about 20 deg along the [011] azimuth. The (110) surface probes the same k–point with a photon energy \( h\nu=27 \) eV and a polar angle of about 35 deg along [T10]. For the (100) surface one starts at \( \Gamma \) for \( k_p=0 \) and reaches X at \( k_p=\sqrt{2}2\pi/\alpha = 2.52\AA \) in Ni (2.46\AA\ in Cu). For the (110) surface the bands are mapped in reverse, starting at X for \( k_p=0 \) and reaching \( \Gamma \) at \( k_p=\sqrt{2}2\pi/\alpha \). This inverted k–scale shows up in Fig. 1 as approximate mirror symmetry of the (100) results (left) and the (110) results (right).

Comparing the intensities near \( \epsilon_f \) one finds opposite behavior for Ni and Cu (Fig. 1 top versus center). The Ni bands fade very quickly below \( \epsilon_f \), whereas the Cu band remains strong and even increases its intensity slightly. Losing oscillator strength so rapidly in Ni presents a puzzle: Where did the spectral weight go that ought to be there according to the sum rule in Eq. 3? Simple technical explanations fail. The \( k \)–acceptance of the analyzer would give equal trends for the Ni–Cu overlayer, establishing them as pure bulk phenomena.

### IV. Possible Explanations for the Anomalies in Ni

Within the framework established in Eqs. 1–4 there are two places where one can search for an explanation of the anomalous behavior of Ni relative to Cu. These are the matrix element \( |M(w,k)|^2 \) and the spectral function \( A(k,\omega) \). As long as one wants to stay within the one–electron picture, the matrix element for excitation of single holes is the natural starting point. We have applied a combined interpolation scheme to the empirical band structures of Ni and Cu for obtaining estimates of \( |M(w,k)|^2 \) [32]. The result describes the (100) data qualitatively, including the opposite intensity trends for Ni and Cu. However, quantitative comparisons are fairly sensitive to the exact location of \( k_F \), and the (110) data are not reproduced well. Clearly, more sophisticated calculations of the photoemission intensity are called for, such as the one–step model with evanescent surface wave functions. In the absence of quantitative calculations we use experimental results for explaining how the matrix element modifies the intensities in Ni and Cu. The key will be a rapid change in the hybridization between the s,p–band and the 3d–bands with energy.

While the \( \Sigma_1 \) conduction band corresponds to the s,p–states in Cu, its symmetry allows for significant d\(_z^2\) character in Ni. The Ni 3d\(_z^2\) states lie close to \( \epsilon_f \) and strongly hybridize with the conduction band, whereas the Cu 3d states lie 2 eV lower. For finding a d–hybridization in Cu comparable to that of Ni one has to look 2 eV lower in energy, as shown in the bottom panels in Fig. 1. The group velocity, i. e., the slope of the Cu conduction band is greatly reduced at this point and has become comparable to that of the Ni. This is the result of an avoided crossing with the d\(_z^2\) level [33]. Likewise, the intensity of the Cu band decreases strongly at these lower energies, similar to Ni below \( \epsilon_f \). The same situation is surveyed in k–space in Fig. 3. Ni and Cu behave similar if one shifts the Ni data to the point of comparable d–hybridization in Cu, i. e., a shift to the left for (100) and to the right for (110).

A calculation of the matrix element [32] for (100) reproduces this effect qualitatively. From such similarities between the Ni bands at \( \epsilon_f \) and the Cu bands at 2 eV below \( \epsilon_f \) we conclude that the intensity changes in Ni are qualitatively consistent with a change in the matrix element due to increasing d–hybridization.

The imbalance between the two spin components can be explained in similar fashion. The minority spin conduction band is more d–like at \( \epsilon_f \) than its majority partner since it hybridizes with the higher–lying minority d\(_z^2\)–level. Therefore,
its matrix element has decreased more than that of the majority band. The consequence is an enhanced spin–polarization at \( \epsilon_f \) which has implications for spin transport phenomena, such as spin–polarized tunneling \([4,5]\) and Andreev reflection at ferromagnetic point contacts \([18,19]\). As mentioned above, the traditional density–of–states model fails to explain the high spin polarization observed in these experiments for Ni. The larger size of the majority spin Fermi surface in Ni would give only 6% spin polarization, compared to the observed 23%–46%. The extra spin–polarization that we find at \( \epsilon_f \) enhances the density–of–states effect and brings theory closer to experiment. For a quantitative comparison it will be necessary to map this polarization across the whole Fermi surface and to replace the photoemission matrix element by the tunneling matrix element.

Despite the qualitative success of the single–particle picture one ought to consider manybody effects in Ni. Excitations of two d–holes are well–documented in this material \([21,22]\). Can they produce an effect similar to the decrease of the matrix element with increasing d–hybridization? There is a scenario where two–hole excitations steal spectral weight from the single–hole band, taking advantage of the sum rule in Eq. 3. It is not unreasonable to assume that the probability for exciting a pair of d–holes increases with the d–character of the band. Therefore, the same arguments as in the previous two paragraphs can be used, where increasing d–character of the band gives rise to a decreasing matrix element. It appears that only quantitative calculations of the matrix element can settle this issue. However, there are some interesting clues pointing towards a contribution of two–hole effects. The intensity drop in Ni is more abrupt than that in Cu at the point of comparable d–hybridization. This is particularly pronounced for the (110) surfaces (Fig. 3, right). One might expect a sharper drop–off for a two–hole process which scales like the square of the d–hybridization. An additional clue comes from the decreasing strength of two–hole excitations across the Periodic Table from Ni to Co and Fe \([23]\). If manybody effects played a role in the spin polarization at \( \epsilon_f \), their influence would gradually fade from Ni to Co and Fe. Such a trend would nicely fit the results from spin–polarized tunneling, where the (one–electron) density–of–states model works best for Fe and worst for Ni \([4]\).

### V. SUMMARY

In summary, we find a rapid loss of spectral weight in the conduction band of Ni below the Fermi level \( \epsilon_f \), which is opposite to the behavior of the analogous band in Cu. Possible mechanisms are considered, such as an increasing lifetime broadening, the single–hole matrix element, and many–hole excitations stealing spectral weight from single–hole excitations below \( \epsilon_f \). The comparison with Cu and a simple estimate of the matrix element indicate that the single–hole matrix element is able to give a qualitative explanation. An additional transfer of spectral weight to two–hole states is quite possible, however. The loss of spectral weight is larger for the minority spin band, thereby enhancing the spin–polarization at \( \epsilon_f \). The photoemission data suggest that similar enhancements of the spin–polarization might occur in magnetotransport and could be used in magnetoelectronic devices. For example, the spin–polarization observed in spin tunneling from Ni exceeds the traditional density–of–states model by a factor of five. The analogy with photoemission suggests that the tunneling matrix element might be responsible.

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[33] For the band topology of Ni along the S axis compare Ref. 15, Fig. 1. The location of the transitions in k space is given in Fig. 4 of Ref. 15. In this transverse geometry the $k_{\perp}$ broadening induced by the finite escape depth is eliminated to first order because the broadenend $k_{\perp}$ component lies tangent to the Fermi surface. Synchrotron radiation was used with p–polarized light incident 600 from the emission direction for the (100) surfaces and 500 for the (110) surfaces, with the sample normal between the photons and electrons. The spectra in Fig. 1 were acquired simultaneously over E,k using a Scienta electron spectrometer. The sample temperature was 200 K, which sharpened the spectral features near $\epsilon_f$ compared to room temperature.
[34] Typical models for $\Gamma(\mathbf{k},\omega)$ contain terms proportional to $\omega^2$ and $T^2$, in addition to a $k^2$ term. These are incorporated into an effective $\Gamma'(\mathbf{k})$, which also takes an experimental broadening into account.

FIG. 1. $E$ versus $k_{\parallel}$ band dispersions of Ni and Cu near the Fermi level $\epsilon_f$, obtained by parallel detection of $E$ and $J$. In Ni, the spectral weight drops rapidly below $\epsilon_f$ (top), in Cu it increases (center). Cu behaves similar to Ni when looking at 2 eV lower energies, where the d–hybridization is comparable (bottom). The $\Sigma_1$ conduction band is mapped from two surfaces at different photon energies in opposite directions (left and right). The gray scale represents high photoemission intensity as dark.

FIG. 2. Photoelectron spectra of Ni(110) and Cu(110) versus $k_{\parallel}$ (symbols, corresponding to vertical cuts in Fig. 1). The lines represent a fit by a Lorentzian spectral function (Eq. 5).

FIG. 3. Spectral weight in Ni and Cu versus $k_{\parallel}$, obtained from the area of the Lorentzian fit in Fig. 2 (Eq. 5). Note the opposite behavior of Ni and Cu near $k_F$.

FIG. 4. Momentum distributions at $\epsilon_f$ for Ni(110) and Ni(100), corresponding to horizontal cuts in Fig. 1 (top). The two spin components of the $\Sigma_1$ conduction band are resolved (arrows). The larger area of the majority spin peak indicates an extra spin–polarization, beyond that expected from the larger size of the majority spin Fermi surface [13].
Energy Relative to $E_F$ (eV)

Ni(100)

Ni(110)

Cu(100)

Cu(110)

$k^\parallel$ along [011] (Å$^{-1}$)

$k^\parallel$ along [110] (Å$^{-1}$)
Ni(100)  

Ni(110)  

Cu(110)  

Cu(100)  

Fit Curve Area  

Fit Curve Area  

$k_F^\uparrow$  

$k_F^\downarrow$  

$k_F^\uparrow$  

$k_F^\downarrow$  

$k$ along [011] (Å$^{-1}$)  

$k$ along [$\bar{1}$ 10] (Å$^{-1}$)  

[1]  

[2]  

[3]  

[4]
Photoemission intensity at $E_F$ along [011] (Å$^{-1}$) and [10] (Å$^{-1}$) for Ni(100) and Ni(110).