Tuning the spin-flip gap in transition-metal magnets by alloying

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We report angle-resolved photoemission measurements of the effects of alloying on the spin-polarized electronic states of ferromagnetic transition metals. We observe that the minimum energy for spin-flip scattering of *d* electrons (the so-called "Stoner gap" in itinerant ferromagnets) is governed by the upper limit of the majority *d* bands. This Stoner gap can be tuned by alloying, which correspondingly alters the polarization of spin currents and lifetime of spin states in designer magnetic alloys for spintronic devices.

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I. INTRODUCTION

Spin electronic (spintronic) devices rely on spin-polarized electric currents for their operation.[1,2] These spin currents are provided by magnetic materials, which have spin-up ($\uparrow$) and spin-down ($\downarrow$) states separated by an exchange energy δE_{EX} at the Fermi energy E_F. The degree to which the overall electron density is spin polarized depends on the number densities of these states, $P=(n_\uparrow-n_\downarrow)/(n_\uparrow+n_\downarrow)$, where $n_\uparrow$ refers to the majority population of states and $n_\downarrow$ refers to the minority population of states at E_F.

In the transition metal magnets Fe, Co, Ni, the valence bands at the Fermi energy are separated into *sp* bands and *d* bands. It is the *d* bands, with the greater effective mass and higher density of states, which carry the local moment. Spin-flip scattering between the highest occupied majority state and the lowest unoccupied minority state, the "Stoner gap," reduces the spin polarization and the lifetime of the spin currents.[3]

A spin-flipping excitation can occur by a vertical ($\Delta k=0$) transition with energy δE_{EX}. Alternatively, a majority-spin electron ($\uparrow$) may enter a minority-spin empty state ($\downarrow$) via an indirect transition requiring a change in wave vector $\vec{k}_{SG}$ with lower change in energy δE_{SG}. The Stoner gap $(\delta E_{SG},\vec{k}_{SG})$ corresponds to the lowest-energy spin-flip excitation.[4]

In this paper, we examine this Stoner gap in the magnetic elements Ni and Co, employing high-resolution imaging of the angle-dependent photoemission out of spin-polarized states. Other authors have measured comparable data for elemental face centered cubic (fcc) Cu,[5,6] fcc Ni,[6,7] and fcc Co.[6,8] The symmetry of states at the Fermi energy defines their dispersive bandstructure. Among the majority *d* bands in the fcc transition metals, the maximum energy in filled bands is reached by the band of symmetry Δ_5 at the *X* point, hence $X_5(\uparrow)$.

Designer magnetic materials, where parameters such as the thickness of a magnetic thin film or the composition of a magnetic alloy can be finely tuned, allow a high degree of customization of spin states.[9] In order to observe changes in the Stoner gap that evolve with alloying (i.e., varying the hole content of the *d* states), we choose to compare the magnetic elements and their alloys with identical (110) oriented fcc crystal structures. In the case of Ni, we chose bulk (110) oriented fcc crystals. In the case of Co, we grew epitaxial fcc thin films on fcc Cu(110) substrates. The exchange splitting is the *d* states, δE_{EX}, along the Δ symmetry direction was measured at the *X* point of the *d* bands. The effect of lightly doping these elements with copper and iron is reported. We observe significant shifts in the *d* bands with alloying, which therefore tunes the spectral distribution of spin-flip excitations.

II. FCC BANDSTRUCTURE

Electrons in a crystal can be completely described by their energy *E*, momentum $\hbar\vec{k}$, the spatial group symmetry, and their spin states. In Ni and Co, the majority ($\uparrow$) *d* electrons lie below E_F for all points $\vec{k}$ in the first Brillouin zone (see the bandstructure in Ref. 1). In Ni, the Stoner gap in the *d* bands spans between the Δ_5 majority spin band maximum near the *X* point and the Fermi energy. This gap widens in fcc cobalt. In fcc Fe, this Stoner gap closes to zero due to the $\Delta_5(\uparrow)$ states breaking through the Fermi level.

The Δ_1 *sp* states hybridize weakly with these *d* states along the ΓX symmetry direction and are weakly spin polarized at E_F. Majority *sp* electrons may scatter into minority *sp* empty states with no change in energy and very little change

in momentum, and so there is no Stoner gap involving these *sp* states. However, the high dispersion and low density of the *sp* states reduces their availability for spin-flip processes.

It is therefore expected that dilute alloying of the transition metals, particularly while maintaining epitaxial thin film structures,[10,11] should allow us to tune the separation of *d* levels and thereby to tune the Stoner gap. This in turn allows us to select the degree of spin-flip scattering, for example, that produced by thermal excitation.

The lifetimes of particles in these states is dependent on the scattering of particles at the Fermi surface, such as by spin flips or spin waves (magnons). The full width at half-maximum (FWHM) energy broadening of states near E_F is related to the lifetime via $\tau=\hbar/\mathrm{FWHM}$. In Ni, many particle excitations (the so-called "6 eV satellite"[12]) reduces the width of the *d* bands, by as much as 40% and the magnetic splitting δE_{EX} by a factor of 2 to 3. This effect weakens in Co and Fe, due to a decrease in the nuclear potential, which serves to delocalize the *d* states and weaken the *d*-*d* interactions.[9] Other processes (experimental resolution, final state broadening) also contribute to increased measured peak width, therefore our measured FWHM is only an upper limit to the inverse lifetime of these states.[13]

III. EXPERIMENTAL

The samples used were single crystals of Ni(110), Cu(110), $Ni_{0.8}Fe_{0.2}$(110), Ni(110) with a small amount of Cu diffused into it ($Ni_{0.96}Cu_{0.04}$), and Co and $Co_{0.81}Cu_{0.19}$ films prepared via molecular beam evaporation (MBE) on a Cu(110) crystal. From previous work, the single crystals are known to provide sharper features near E_F than epitaxial thin films.[10,14,15] The single crystals were prepared by annealing in 100 Torr H_2 for several days to remove bulk impurities with temperature ramping from 500 °C to 850 °C, the removal of segregated impurities by repolishing, electropolishing in a chromic acid solution,[16] and sputter annealing up to 800 °C. For the $Ni_{0.96}Cu_{0.04}$ sample a "diffusion method" was used[14] in which approximately 9 Å of Cu was deposited by MBE and then the sample annealed above the 500 °C Ni bulk diffusion temperature. This results in a perfect fcc crystalline structure with a negligible concentration gradient over the probing depth of 5–10 Å. The quality of all samples was checked with RHEED during MBE growth and LEED afterward. The stoichiometry was determined *in situ* by taking the areas of the 3*p* core level peaks at a photon energy $h\nu=170$ eV and including minor corrections for the cross section and for the energy-dependent transmission of the spectrometer. Stoichiometry uncertainty is approximately ±1%.

Experiments were performed at the SRC synchrotron facility where photoemission spectra were obtained using an electron spectrometer with energy and angle multidetection, and undulator-produced *p*-polarized synchrotron radiation. The experimental geometry was optimized for an imaging bandstructure near *X* in momentum space. By using angle-resolved photoelectron spectroscopy (ARPES) with synchrotron radiation of variable photon energy and detection angle, we can probe the dispersion at different momenta $\vec{k}$ within the Brillouin zone. In this work, a photon energy of 15 eV was used, which corresponds to the *X* point for normal emission from the fcc (110) surface. Small variations in detection angle away from normal in the [100] direction corresponds to band dispersions along $X-\Gamma$ in the Δ direction.

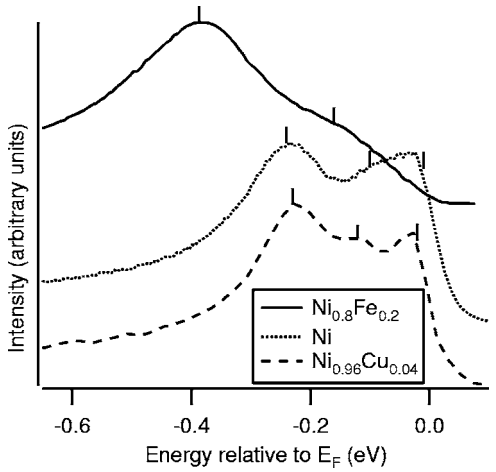

FIG. 1. EDCs of occupied electron states at X for Ni and Ni alloys, with $h\nu=15$ eV. Tick marks indicate the position of the Doniach-Sunjic-shaped peaks.

IV. RESULTS AND DISCUSSION

Figure 1 shows energy distribution curves (EDC) at *X* on crystals of $Ni_{0.8}Fe_{0.2}$, Ni, and $Ni_{0.96}Cu_{0.04}$. The peaks can be fitted by Lorentzians with Doniach-Sunjic asymmetric lineshape to reflect secondary (two-electron) effects.[17] All peaks within a single EDC have been fit with identical Doniach-Sunjic asymmetry parameter α, and multiplied against the Fermi-Dirac distribution function to simulate the filling of states at the Fermi energy.

The X_2 and X_5 states have different matrix elements due to their different crystal symmetries depending on the crystal orientation relative to the polarization of the linearly polarized photons. In this measurement geometry, we used *p*-polarized light which preferentially excites electrons from the X_2 states.

The experimental data is presented in Table I. Consider the single crystal samples $Ni_{0.96}Cu_{0.04}$, Ni, and $Ni_{0.8}Fe_{0.2}$ (Permalloy): since the minority $X_2^{\downarrow}$ state essentially lies at or above E_F for these samples, the X_2 Stoner gap is equal to the $X_2^{\uparrow}$ binding energy. We see that the FWHM increases as one progresses from Cu to $Ni_{0.96}Cu_{0.04}$ to Ni to $Ni_{0.8}Fe_{0.2}$, adding *d* holes to the system. The X_2 Stoner gap likewise increases with added *d* holes. Nonmagnetic pure Cu is an exception, as it has a very different inner potential relative to the magnetic alloys. An exchange splitting does not appear in Cu until after it has been alloyed to roughly $Cu_{0.4}Ni_{0.6}$ and the *d* bands have risen to meet the Fermi level.[18] As *d* holes are added to the metal by alloying, the exchange splitting widens, the majority *d* bands move below the Fermi level, and the minority *d* bands shift upward in energy through the Fermi level and empty themselves of electrons.

For the two epitaxially grown films, Co/Cu(110) and $Co_{0.81}Cu_{0.19}$/Cu(110), we unexpectedly find that Co (with a

TABLE I. Measured bandgap at X in thin film (†) and crystalline (*) samples. Binding energy (BE) of the peaks is shown alongside the full width at half-maximum (FWHM), with uncertainty at the last digit in brackets. The majority X_5 peak was not measurable in the thin films.

	Majority X_2		Majority X_5		Minority X_2	
Sample	BE (eV)	FWHM	BE (eV)	FWHM	BE (eV)	FWHM
$Co(110)^{\dagger}$	0.30(1)	0.148(7)		—	Unoccupied	
$Co_{0.81}Cu_{0.19}(110)^{\dagger}$	0.317(3)	0.441(3)		—	Unoccupied	
$Ni_{0.8}Fe_{0.2}(110)^{*}$	0.386(5)	0.244(4)	0.160(5)	0.26(1)	Unoccupied	
$Ni(110)^{*}$	0.24(2)*	0.166(4)	0.10(2)	0.10(1)	0.01(2)	0.093(3)
$Ni_{0.96}Cu_{0.04}(110)^{*}$	0.23(2)*	0.127(6)	0.12(2)	0.10(1)	0.02(2)	0.064(3)
$Cu(110)^{*}$	2.35(1)	0.0996(4)	2.01(1)	0.049(1)	Not exchange split	

greater number of d holes) has a smaller X_2 Stoner gap than $Co_{0.81}Cu_{0.19}$. The very large FHWM for $X_2^{\uparrow}$ in $Co_{0.81}Cu_{0.19}$ is likely due to bad surface morphology in the epitaxially grown thin film alloy. The X_5 peak proved too weak to be measurable in these MBE-deposited films. The larger X_2 Stoner gap in $Co_{0.81}Cu_{0.19}$/Cu(110) is probably because of lattice mismatch strain in the epitaxially grown thin film samples. In the first place, variation in the separation between lattice sites changes the overlap between adjacent orbitals and can therefore distort the resulting crystal bandstructure, for example.[19] Furthermore, distortions in the perpendicular and in-plane lattice constants lead to distortions in the size of the first Brillouin zone, which can lead to changes in the bandstructure, especially at the high symmetry points. For example, the X point occurs at $2\pi/a$, where a is the (varying) lattice constant. Nonetheless, the X_2 Stoner gap is wider for Co than Ni, in line with our expectations. Our measurements for the elemental films agree well with previous measurements by other groups.[5–8]

V. CONCLUSION

In summary, we have examined the band structures of the magnetic elements Ni, Co, and Fe along the same ΓX symmetry direction of fcc crystals, and reported the effect on the Stoner gap (minimum spin-flip excitation) when varying the number density of d holes through alloying. For d electrons with Δ_2 spatial group symmetry, the Stoner gap is observed to increase with increasing number of d holes (replacing Ni atoms with Fe). This Stoner gap also decreases when the number of d holes is decreased (replacing Ni atoms with Cu). The Stoner gap is greater in elemental Co than Ni. In Fe, the Stoner gap reduces to zero for these Δ_2 symmetry states.

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