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Room temperature spin Kondo effect and intermixing in Co/Cu non-local spin valves

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The anomalous low temperature suppression of the spin accumulation signal $\Delta R_{NL}$ in non-local spin valves (NLSVs) based on common ferromagnet (FM)/normal metal (N) pairings has recently been shown to result from a manifestation of the Kondo effect. Local magnetic moments in the N due to even minor levels of FM/N interdiffusion depolarize the injected spin current, suppressing the effective spin polarization around and below the Kondo temperature $T_K$. Previous studies have focused on FM/N combinations that happen to have low $T_K$ so that Kondo effects occur only well below 300 K. Here, we study NLSVs based on Co/Cu, a materials combination that is not only technologically relevant but also has a high $T_K$, up to 500 K. Despite the negligible equilibrium solubility of Co in Cu, we find clear Kondo effects in both $\Delta R_{NL}$ and Cu resistivity, due to Co/Cu intermixing that we probe via quantitative transmission electron microscopy. Most significantly, under certain conditions the spin Kondo effect suppresses the injected spin polarization even at room temperature, with important technological implications. Studies as a function of the Cu thickness and annealing temperature reveal complex trends in interdiffusion lengths and Kondo effects, which we interpret in terms of the interplay between diffusion kinetics and thermodynamics, as well as the thickness dependence of the Kondo effect. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4984896]

Non-local spin valves (NLSVs)1,2 efficiently separate charge and spin currents, allowing for the study of a wide variety of spin transport phenomena. These devices are also of interest for application as magnetic field sensors in hard disk drives, with several potential advantages over tunneling magnetoresistance devices.3–5 In essence, an NLSV is simply a disk drive with the resulting Kondo relaxation leading to depolari-
tion of the two electrodes. A long-standing puzzle in metal-
lic NLSVs has been the widely observed suppression of the
spin accumulation, and a corresponding non-local voltage
$V_{NL}$ for common FM/N pairings, i.e., non-monotonic
$\Delta R_{NL}(T)$.6–18 This is in apparent contrast to predictions based
on Elliott-Yafet (EY) spin relaxation in pure N metals with
low spin-orbit coupling,19–21 where the spin relaxation time,
and hence $\Delta R_{NL}$, should increase monotonically on cooling.

Recent work has shown that the suppression of $\Delta R_{NL}$ at
low $T$ is due to FM impurities forming local moments in the
N,11 with the resulting Kondo relaxation leading to depolariza-
tion of the injected spin current. This depolarization
increases logarithmically on cooling through the Kondo tem-
perature $T_K$ of the FM/N pair. This manifestation of the
Kondo effect has now been observed in NLSVs in which the
Kondo impurities diffuse into the N from the FM contacts,11,13
as well as those in which the magnetic impurities are intro-
duced throughout the N channel.12,16 In the former case, local
moments near the interface reduce the polarization $z$ of the
injected current. This can be quantitatively described by an
extension of the Valet-Fert model accounting for spin relaxa-
tion at local moments.23 In the latter case, local moments
throughout the N lead to additional “bulk” spin relaxation,
reducing the spin diffusion length $\lambda_N$. The Kondo-induced
non-monotonicity in $\Delta R_{NL}(T)$ can be eliminated by using an
N material incapable of supporting local moments for transi-
tion metal FMs,11 such as Al,22,24,25 or by inserting a thin
layer of such a material at the FM/N interface.11

In this work, we explore these “spin Kondo effects” (by
which we mean $T$-dependent suppressions of the effective
polarization or spin diffusion length by Kondo spin relaxation
at magnetic impurities) in NLSVs fabricated from Co/Cu, an
FM/N pairing that has not yet received detailed examination.
This is despite the technological relevance of this pairing,
which arises due to the widespread use of Cu as an N layer in
spintronic devices, and the high Curie temperature, spin polar-
ization, and anisotropy of Co-based alloys. More important in
the current context, Co in Cu possesses a $T_K$ of 500 K, i.e.,
well above ambient.26–29 Utilizing measurements over a wide
range of Cu thicknesses (50–200 nm) and annealing tempera-
tures $T_A$ of 80–500 °C, we show that the spin Kondo effect
is clearly manifested in $\Delta R_{NL}(T)$ in Co/Cu NLSVs, despite
the negligible equilibrium solubility of Co in Cu.30 The $d$ depen-
dence of $\Delta R_{NL}$ confirms that this is an interface effect, with
only modest Co/Cu intermixing leading to low $T$ suppression of
$z$ of up to 40%. Most significantly, and with technological

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ramifications, the Kondo suppression of $z$ in Co/Cu can extend to room temperature. Through complementary Scanning Transmission Electron Microscopy/Energy Dispersive X-ray Spectroscopy (STEM/EDX), we also describe and interpret a non-monotonic $T_A$ dependence of the charge and spin Kondo effects. The suppression of spin accumulation at high $T$ and the non-monotonic $T_A$ dependence are in contrast to Fe/Cu NLSVs, due to the larger $T_K$ for Co in Cu, as well as the very different miscibilities of the two pairings.

NLSVs [see Fig. 1(a) for device geometry] were fabricated on Si/Si-N substrates by ultra-high vacuum electron beam evaporation of high purity Co and Cu, multi-angle shadow evaporation, enabling single-shot deposition of low resistance (transparent) interfaces. The thickness $t_N$ of the Cu channels ranged from 50 to 200 nm (with a width of 100–150 nm), while the Co thickness $t_F$ was 16 nm (with widths of 100–150 nm). More details on fabrication, device characterization, and interface resistance are given in the supplementary material (Figs. S1 and S2). Annealing was performed in vacuum ($\sim10^{-8}$ Torr) for 2 h at either 300 or 500 °C. Unannealed devices were exposed to $\sim80^\circ$C during lift-off and are thus designated by $T_A = 80^\circ$C. Transport measurements were performed using a 13 Hz ac excitation of 316 µA in a continuous flow cryostat with a superconducting magnet.

Figure 1(b) shows the channel resistivity $\rho_N(T)$ for three different $t_N$ values for illustrative $T_A$ values of 80 °C (solid lines) and 300 °C (dashed lines). The behavior is as expected, $\rho_N$ decreasing with increasing $t_N$ and upon annealing at 300 °C; the lowest $\rho_N$ achieved is below 0.5 $\mu$Ω cm. $\Delta R_{NL}(T)$ was measured for a range of separations $d$ from 150 to 2000 nm. Figure 1(c) shows the results at $d = 250$ nm for both the $T_A = 80^\circ$C and 300 °C devices for the three $t_N$ values studied. Note the clear non-monotonicity of $\Delta R_{NL}(T)$ for all $t_N$; the spin signal increases with decreasing $T$ before reaching a maximum at $T_{max}$ [arrows in Fig. 1(c)]. $\Delta R_{NL}$ then drops below $T_{max}$, with a decrease of up to 45% (relative to the peak) by 5 K in annealed devices. $T_{max}$ is notably dependent on $T_A$ and $t_N$, increasing as $T_A$ is increased to 300 °C and as $t_N$ is reduced. These features immediately suggest Kondo spin relaxation, with the relatively high $T_{max}$ potentially reflecting the high $T_K$ for Co in Cu.

Looking in more detail, in these NLSVs, $\Delta R_{NL}$ is $T$-dependent for two reasons. First, the effective polarization $\mathcal{z}_{eff}$ of the injected current varies due to the $T$ dependence of the current polarization $\mathcal{z}_{FM}$ of the Co, as well as any spin-dependent processes at the FM/N interface. We thus use $\mathcal{z}_{eff}$ in place of $\mathcal{z}_{FM}$ to account for potential Kondo suppression at the interface. Second, in the EY mechanism, the spin relaxation rate scales with the $T$-dependent momentum relaxation rate, leading to $T$-dependent $\lambda_N$. We thus separate $\lambda_N(T)$ and $\mathcal{z}_{eff}(T)$ by fitting $\Delta R_{NL}(d, T)$ to a 1-D solution of the Valet-Fert model for NLSVs in the transparent limit

$$\Delta R_{NL} = \frac{4 \mathcal{z}_{eff}^2 R_F^2}{(1 - \mathcal{z}_{eff}^2)^2 R_N^2} e^{-d/\lambda_N}$$

where $R_F = \rho_F \lambda_F/A_I$ and $R_N = \rho_N \lambda_N/A_N$ are the spin resistances of the FM and N. Here, $A_I$ is the area of the FM/N interface, $A_N$ is the channel cross-section, and all dimensions are measured by scanning electron microscopy. $\rho_N(T)$ is shown in Fig. 1(b), and the Co resistivity $\rho_F$ is measured on nanowires with identical dimensions to those in the NLSVs. We approximate the FM spin diffusion length $\lambda_F \approx 4$ nm, utilizing an empirical scaling relation between $\lambda_F$ and $\rho_F$ (27 $\mu$Ω cm at 295 K in our case).

Fitting for the only remaining parameters, $\lambda_N$ and $\mathcal{z}_{eff}$, distinguishes whether the low $T$ suppressions in $\Delta R_{NL}(T)$ in Fig. 1(c) originate from spin relaxation throughout the channel [i.e., in $\lambda_N(T)$], depolarization at the interface [i.e., in $\mathcal{z}_{eff}(T)$], or both. Figs. 2(a) and 2(b) show $\Delta R_{NL}(d)$ at several $T$ values between 10 and 275 K for $t_N = 200$ nm and $T_A = 80^\circ$C. Fits to Eq. (1) are shown as solid lines. For $T_A = 80^\circ$C [Fig. 2(a)], $\Delta R_{NL}(d)$ is well-described by

![Figure 1](image-url)
Eq. (1). For $T_A = 300 \, ^\circ C$ [Fig. 2(b)], however, $\Delta R_{NL}$ at low $d$ ($\leq 350 \, \text{nm}$) may potentially show slight deviations from Eq. (1), as seen in annealed Fe/Cu NLSVs and attributed to interfacial Kondo relaxation.\textsuperscript{13} Nevertheless, from the high $d$ behavior, annealing at $300 \, ^\circ C$ clearly increases $\lambda_N$, as indicated by the decreased slope of $\Delta R_{NL}(d)$ on this semi-log plot. Figs. 2(c) and 2(d) show the equivalent data for $t_N = 50 \, \text{nm}$ for $T_A = 80$ and $300 \, ^\circ C$. These lower $t_N$ devices have reduced $\lambda_N$ (as expected from $\rho_N$) and thus provide a smaller range of $d$ over which $\Delta R_{NL}$ remains above the noise floor. This limits our ability to separate $\alpha_{eff}$ and $\lambda_N$ in this limit. For this reason, we fit the results on the $t_N = 50 \, \text{nm}$ and $T_A = 80 \, ^\circ C$ devices using a $\lambda_N$ value with a $T$ dependence constrained by $1/\rho_N(T)$ (via EY scaling); $\lambda_N(T)$ indeed follows such scaling in higher $t_N$ devices. More details are given in the supplementary material (Fig. S3).

The primary results of this work are shown in Figs. 3(a)–3(f), where we compare the extracted $\alpha_{eff}(T)$ and $\lambda_N(T)$ for all $t_N$ and $T_A$. By normalizing $\alpha_{eff}(T)$ to its maximum, $\alpha_{eff,max}$, we compare the magnitude and onset $T$ of the Kondo suppression of spin polarization as a function of $t_N$ and $T_A$. The absolute values of $\alpha_{eff}(T)$ are given in Fig. S4 of the supplementary material [Fig. S5 also provides normalized $\Delta R_{NL}(T)$ data for reference]. At $T_A = 80 \, ^\circ C$ [black squares in Figs. 3(a)–3(c)], $\alpha_{eff}(T)$ first increases upon cooling, before reaching a broad maximum and then dropping by 10%–20% relative to $\alpha_{eff,max}$. Qualitatively, this is as anticipated from Fig. 1(c). At $T_A = 300 \, ^\circ C$, however [red circles in Figs. 3(a)–3(c)], the behavior is different, and $\alpha_{eff}$ continuously decreases on cooling, such that by 5 K $\alpha_{eff}$ is suppressed by up to 40% relative to $\alpha_{eff,max}$. Increasing $T_A$ to $500 \, ^\circ C$ [green triangles in Figs. 3(a) and 3(b)] then induces only small changes compared to $300 \, ^\circ C$. The low $T$ decrease in $\alpha_{eff}$ saturates at around 35%, with the $t_N = 100 \, \text{nm}$ data even suggesting a non-monotonic $T_A$ dependence at low $T$.

Non-monotonicity with respect to $T_A$ is also seen in $\lambda_N$ [Figs. 3(d)–3(f)], which first increases on annealing at $300 \, ^\circ C$, before decreasing at $500 \, ^\circ C$. At a given $T_A$, $\lambda_N(T)$ monotonically increases on cooling, however (as expected from EY relaxation), with the only exception being $t_N = 200 \, \text{nm}$ and

![Fig. 2. Spin accumulation signal $\Delta R_{NL}(T)$ vs. the injector/detector separation $d$ for channels of thickness $t_N = 200 \, \text{nm}$ (top panels) and 50 nm (bottom panels). Data shown for as-deposited [$T_A = 80 \, ^\circ C$ (a) and (c)] and after annealing [$T_A = 300 \, ^\circ C$ (b) and (d)], at multiple measurement $T$ between $10$ and $275 \, K$. Solid lines are fits to Eq. (1)].

![Fig. 3. Temperature ($T$) dependence of the effective injected spin polarization normalized to its maximum ($\alpha_{eff}/\alpha_{eff,max}$, top panels) and the spin diffusion length in the non-magnetic channel ($\lambda_N$, bottom panels). Data are shown for channel thicknesses ($t_N$) of 200 nm (left), 100 nm (middle), and 50 nm (right). The results for $T_A = 80$, 300, and 500 $^\circ C$ are shown. First and last data points show the representative error bars on each dataset.]}
$T_A = 300 \degree C$, where a small decrease occurs at low $T$. We thus conclude that the low $T$ downturns in $\Delta R_{NL}$ in Fig. 1(c) are due to the suppression of $x_{eff}(T)$, as opposed to $\Delta x(T)$, similar to other FM/N combinations studied by these means.\textsuperscript{11,13} The additional spin relaxation at low $T$ in Co/Cu NLSVs is therefore interfacial, derived from Kondo spin relaxation at local moments near the FM/N interface. This is in contrast to naive expectations based on equilibrium immiscibility of Co and Cu, as returned to below. Most significantly, at $T_A = 300 \degree C$, we find no clear saturation or peak in $x_{eff}(T)$, even up to 275 K. This indicates that the spin Kondo effect in Co/Cu NLSVs can be active even at room temperature. In contrast, previous studies of Kondo effects in NLSVs focused on FM/N pairings with $\Delta T$\textsubscript{K} (TK) \textsuperscript{22,24}07-4 Watts and $\Delta C$, where $\Delta C$ is the magnetic impurities are indeed present in the bulk of the Cu channel. These data were fitted with an empirical model for the Kondo effect\textsuperscript{38} for $\rho_N(T)$ due to the charge Kondo effect is clear in the $T = 200 \\text{nm}$ and $T_A = 80 \degree C$ devices [solid circles in Fig. 4(d)], indicating that atomic-scale magnetic impurities are indeed present in the bulk of the Cu channel. These were fitted with an empirical model for the Kondo effect\textsuperscript{38}

$$\rho_N = \rho_0 + AT^s + \rho_K \left( \frac{T_{K'}^2}{T^2 + T_{K'}^2} \right)^s,$$

where $\rho_0$ is the residual resistivity, $AT^s$ captures electron-phonon scattering, $\rho_K$ is the Kondo resistivity, and $T_{K'} = T_K / \sqrt{2^{3/s} - 1}$. For a spin $1/2$ impurity, $s = 0.225$, but this is expected to decrease as the spin of the Kondo impurity increases.\textsuperscript{39} In our case, we obtain a good fit with $s = 0.225$, using the reported Co in bulk Cu $T_K$ of 500 K.\textsuperscript{26-29} The data are thus consistent with this high $T_K$ although, as always with high $T_K$ systems, phonon scattering results in little sensitivity to the exact $T_K$. The extracted $\rho_K = 12 \\text{n}\Omega \\text{cm}$ for $T_A = 80 \degree C$ increases to 14 \text{n}\Omega cm for $T_A = 300 \degree C$ [Fig. 4(e)], indicating increased $C_{Co}$ in the channel. This is concurrent with strengthening of the spin Kondo effect in $x_{eff}(T)$ [Figs. 3(a)–3(c)]. At $T_A = 500 \degree C$, however [Fig. 4(f)], the charge Kondo effect abruptly diminishes ($\rho_K = 1 \\text{n}\Omega \\text{cm}$), again indicating a non-monotonic response to $T_A$.

Considering these STEM/EDX and $\rho_N(T)$ data, along with the trends in spin transport from Figs. 1(e) and 3(a)–3(c), a consistent interpretation emerges. First, these as-deposited Co/Cu NLSVs must clearly contain kinetically trapped Co atomic impurities, with non-negligible intermixing at the Co/Cu interface. $x_{eff}(T)$ and $\ell_{Co}$ [Figs. 3(a) and 4(a)] show that this is true near the interface, with $\rho_N(T)$...
Although higher energy than evaporation, sputtering can result in Cu–Co solid solution films with remarkably high $x$. We propose that similar effects occur here on a smaller scale, enabling Co/Cu mixing. Annealing at 300°C increases diffusion, resulting in stronger charge [Figs. 4(d) and 4(e)] and spin [Figs. 3(a) and 3(b)] Kondo effects. At $T_A$ $\approx$ 500°C, however, the dramatic changes signal a return to the equilibrium behavior (i.e., Co/Cu segregation) that must occur at sufficiently high $T_A$. STEM/EDX then shows segregation along large length scales [Fig. 4(c)], with $\rho_N(T)$ indicating negligible charge Kondo effect [Fig. 4(f)]. $\ell_C$ also decreases at this point, the low $T$ Kondo suppression in $\sigma_{xx}(T)$ saturating, or even becoming non-monotonic with $T_A$. One final issue is the $t_N$ dependence of these Kondo effects. For $t_N$ $\lesssim$ 100 nm, the Kondo effect in $\rho_N(T)$ is negligible at all $T_A$ [Figs. 4(d)–4(f)], despite clear spin Kondo effects [Figs. 1(c) and 3(a)–3(c)]. A potential explanation for this can be found in the literature on thin film dilute Ni$_x$FM, alloys, where the weakening of the Kondo effect with decreasing thickness is widely reported and ascribed to spin-orbit-induced surface anisotropy. The fact that a pronounced spin Kondo effect remains in our Co/Cu NLSVs even at low $t_N$ again highlights the sensitivity of this effect to the FM/N interface.

In conclusion, despite equilibrium immiscibility, Co/Cu NLSVs exhibit strong effects of Kondo spin relaxation due to interfacial mixing. These reach a maximum at 300°C annealing, at which point the Kondo suppression of the effective injected spin current polarization is as much as 40%, persisting even to room temperature, with clear technological implications. Elimination of this effect could employ an N channel or FM/N interlayer metal that does not support local magnetic moments, such as Al. Finally, the spin and charge Kondo effects in these devices exhibit complex trends with the channel thickness and annealing temperature, which can be interpreted in terms of the interplay between Co/Cu diffusion kinetics and thermodynamics, and the known thickness dependence of the charge Kondo effect.

See supplementary material for additional details on device fabrication and characterization, absolute spin polarizations, and normalized spin signals, as well as a discussion of fitting procedures for 50-nm-thick channels.

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