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Quenching of impurity spins at Cu/CuO interfaces: An antiferromagnetic proximity effect

Ko Munakata,* Theodore H. Geballe, and Malcolm R. Beasley
Department of Applied Physics, Stanford University, Stanford, California 94305, USA and
Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, USA
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It is observed that the magnetoconductance of bilayer films of copper (Cu) and copper monoxide (CuO) has distinct features compared to that of Cu films on conventional band insulator substrates. We analyze the data above 2 K by the theory of weak antilocalization in two-dimensional metals and suggest that spin-flip scattering by magnetic impurities inside Cu is suppressed in Cu/CuO samples. Plausibly the results imply a proximity effect of antiferromagnetism inside the Cu layer, which can be understood in the framework of Ruderman-Kittel-Kasuya-Yoshida interactions. The data below 1 K, which exhibit slow relaxation reminiscent of spin glass, are consistent with this interpretation.

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As the technology to synthesize high-quality thin films and thin-film interfaces steadily improves, there has been an extensive search for different physical properties in thin-film heterostructures in the condensed-matter physics community. In fact, numerous heterostructure interfaces have been found to exhibit unique phenomena that are not present in bulk materials. Some prominent examples include the exchange-bias effects in antiferromagnet/ferromagnet interfaces,[1] high-mobility two-dimensional electron gases in semiconductor and complex oxide heterostructures,[2,3] and various proximity effects. The proximity effect at solid-state interfaces can be defined as a mutual induction of certain physical properties from one material into an adjacent one across their interface. The most famous example is that of superconductivity, where superconducting pairs are induced in a neighboring normal metal while normal electrons in the metal permeate the superconductor.[4,5]

At the interfaces between a metal and a nonsuperconducting material, especially an insulator, one might naively expect no proximity effect besides a simple transfer of charges and development of a Schottky barrier. In this Rapid Communication, however, we present evidence for a unique proximity effect that arises between a normal metal and an antiferromagnetic (AF) charge-transfer insulator. Specifically, we show evidence for the creation of AF spin ordering in a normal metal due to the proximity effect through spin-spin interactions with an AF charge-transfer insulator. The existence of such a proximity effect has been anticipated theoretically.[6] The heterostructure of a copper (Cu) thin film and a copper monoxide (CuO) thin film was synthesized as a potential model system for such a proximity effect.[9] This Cu/CuO bilayer exhibits distinct features in magnetotransport compared to a Cu thin film on a conventional band insulator substrate. The magnetoconductance of both films above 2 K can be analyzed by the theory of weak antilocalization and indicates the quenching of spin-flip scattering by magnetic impurities inside the Cu in proximity to CuO. This nonlocal effect in magnetotransport by an AF insulator can be naturally interpreted as a consequence of AF spin ordering induced in the Cu.

Our copper monoxide (CuO) films were synthesized on magnesium oxide (MgO) substrates using electron-beam evaporation. An ultrasonically cleaned MgO (001) substrate was annealed first at 500 °C in vacuum for a few hours and further at 750 °C under rf-excited atomic oxygen flux[14] for 10 min. A few nanometers of homoepitaxial MgO were then deposited by pulsed laser deposition using a Mg target under the atomic oxygen flux, which yielded a very smooth and chemically clean MgO surface. Following the cleaning procedure, the substrates were cooled to 500 °C, where Cu was deposited using electron beam evaporation under atomic oxygen to synthesize a 21-nm CuO film. After the deposition of CuO, the sample was cooled to room temperature under plasma-excited atomic oxygen flux. The atomic oxygen flux was then turned off and a 3-nm Cu film was deposited in vacuum by electron beam evaporation. As a comparison, we also synthesized 3-nm Cu films using the same Cu source on several different band insulator (BI) substrates (MgO, Al_2O_3, Si), which we collectively call Cu/BI films because all the films behaved in a similar way in the transport measurements. The transport properties were measured with a Quantum Design Physical Property Measurement System.

Using x-ray diffraction, we found that the (111) direction of our CuO film is aligned parallel to the (001) direction of the MgO substrate, similar to that observed by others.[15] Although the CuO film is not single crystalline due to the twinning of CuO with respect to MgO, the (111) peak of the x-ray diffraction is sharp with a full width at half maximum (FWHM) of the rocking curve of less than 0.2°, suggesting good crystalline quality. In addition, atomic force microscopy shows that the rms roughness of the surface is only ∼0.5 nm, which makes it possible to synthesize an ultrathin continuous Cu film on top of the CuO.

Figures 1(a) and 1(b) represent the sheet resistance of Cu/CuO and Cu/MgO films, respectively, as functions of temperature. While the resistance of both films above 50 K increases with temperature, as expected for a simple metal, both samples have a minimum in the sheet resistance ∼50 K. In order to further examine the transport properties of the two films, we show in Figs. 2(a) and 2(b) the sheet conductance as a function of external magnetic field H perpendicular to the films at different temperatures between 2 and 10 K. In both samples, the magnetoconductance is negative at fields lower than ∼0.4 T and positive at higher fields, which become more evident at lower temperatures.

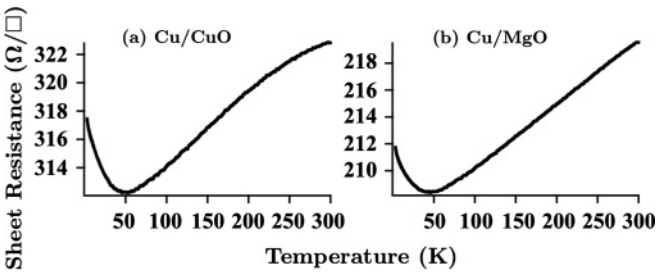

FIG. 1. Temperature dependence of sheet resistance of (a) the Cu/CuO and (b) the Cu/MgO films. The deviation from the straight line above 200 K in (a) is due to the resistance of CuO.

These transport properties in two-dimensional metallic systems such as Cu are well known and were extensively examined since the late 1970's, and were attributed to a weak localization and antilocalization effect.[16–20] In fact, since CuO and band insulators have much higher resistance at these temperatures than Cu, the current must predominantly flow inside the Cu. This consideration, together with the fact that both Cu films were deposited from the identical, fully melted Cu source using the same e-beam system, reasonably suggests that there should be no large difference between the transport properties of Cu/CuO and Cu/BI films. However, Fig. 2 also shows a large difference in the detailed shapes of the curves: The negative component of the magnetoconductance at magnetic fields lower than 0.4 T is much more prominent in the Cu/CuO film than in the Cu/MgO film. This is the essential experimental finding in this Rapid Communication.

In order to examine the origin of this difference, we analyze the data by fitting the magnetoconductance curves to the theoretical equation for the weak antilocalization effect:[16,18,21]

$$\frac{\Delta\sigma(H)}{\sigma_0} = -\frac{3}{2}\left\{\ln\frac{\frac{4}{3}H_1 + H_2}{H} - \psi\left(\frac{1}{2} + \frac{\frac{4}{3}H_1 + H_2}{H}\right)\right\} + \frac{1}{2}\left\{\ln\frac{H_2}{H} - \psi\left(\frac{1}{2} + \frac{H_2}{H}\right)\right\}.$$

In the above equation, $\Delta\sigma(H)$ is the difference in sheet conductance between the value under a magnetic field H and the zero-field value. There are two fitting parameters $H_1 \equiv H_{so} - H_s$ and $H_2 \equiv H_i + 2H_s$, where $H_i \equiv \hbar/4eD\tau_i$ is the effective field proportional to the inelastic scattering rate $1/\tau_i$, $H_s \equiv \hbar/4eD\tau_s$ is proportional to the spin-flip scattering rate $1/\tau_s$, and $H_{so} \equiv \hbar/4eD\tau_{so}$ is proportional to the spin-orbit scattering rate $1/\tau_{so}$. $\sigma_0 \equiv e^2/\pi h \simeq 1.23 \times 10^{-5}$ S is a constant with the unit of conductance, D is the diffusion constant for electron motion inside Cu films, and ψ is the digamma function. We emphasize that this formula and its relatives have been successfully applied to many metallic thin films[17,18] as well as two-dimensional electron gas systems,[22,23] which supports the reliability of our analysis.

We note that neither the Kondo effect[24] nor the electron-electron interaction in a disordered system[25] significantly affects our analysis. The possibility of the Kondo effect is in fact ruled out by the observation that the magnetoconductance in the fields parallel to the surface is weak and negative and thus very different from that in the perpendicular fields. Moreover, the minimum of resistivity of a slightly thicker film occurs at a lower temperature, which is in contrast to the Kondo effect. As for the effect of electron-electron interactions, it is probable that, as shown by Ref. 20, the temperature dependence of sheet resistance in Fig. 1 does include a significant contribution from this effect. However, it does not affect the results of our analysis using low-field magnetoconductance.

We examine the temperature dependence of the different scattering rates by fitting the experimental curve at each temperature by the theoretical equation. Figure 3(a) represents the temperature dependence of H_1, which is related to the spin-orbit and spin-flip scattering rates. The two films have similar values in H_1, which do not seem to have a significant temperature dependence. Since both the spin-orbit scattering and the spin-flip scattering are expected to be temperature independent,[26] the experimental results that H_1 does not exhibit large temperature dependence assure the validity of our analysis.

On the other hand, the temperature dependence of H_2, as shown in Fig. 3(b), demonstrates the clear difference in transport properties between Cu/CuO and Cu/MgO films. While at temperatures higher than 10 K both films show a similar decrease of H_2 as the temperature decreases, the decrease of H_2 of the Cu/MgO becomes much slower than

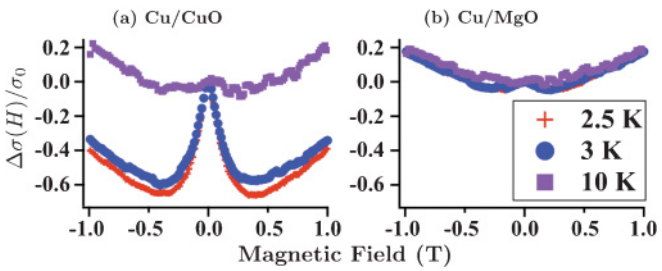

FIG. 2. (Color online) Normalized magnetoconductance at 2.5, 3, and 10 K of (a) the Cu/CuO and (b) the Cu/MgO films. $\Delta\sigma(H)$ is the difference in sheet conductance between the value under a magnetic field H and the zero-field value, while $\sigma_0 \equiv e^2/\pi h \simeq 1.23 \times 10^{-5}$ S is a constant for the normalization.

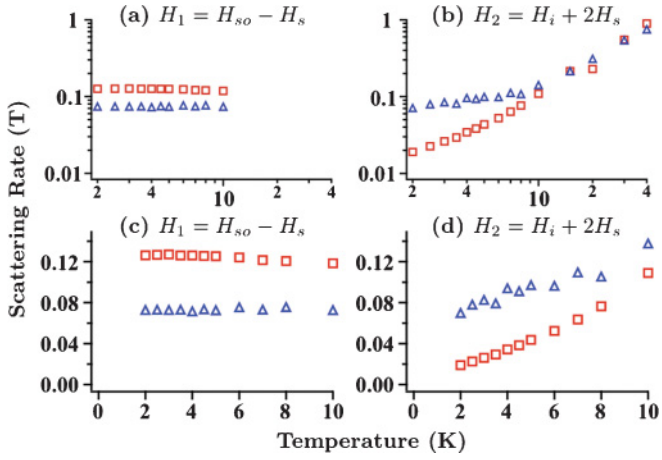

FIG. 3. (Color online) Temperature dependence of (a) H_1 in a log scale, (b) H_2 in a log scale, (c) H_1 in a linear scale, and (d) H_2 in a linear scale. In each figure, squares represent the Cu/CuO film, while triangles represent the Cu/MgO film.

TABLE I. Concentrations of trace magnetic impurities in ppm in a 300-nm-thick Cu film measured by SIMS. We note that the measured concentration is accurate only up to a factor of ∼2, due to our rough estimate of sensitivity factors.

^{51}V	^{52}Cr	^{55}Mn	^{56}Fe	^{58}Ni	^{59}Co	^{102}Ru
0	0.1	1	2	2	4	0

that of the Cu/CuO film below 10 K. In fact, the saturation of the decrease in H_2 in thin metallic films including Cu has been observed in previous studies by other researchers.[17,18] Since H_2 is a weighted sum of inelastic and spin-flip scattering rates, the saturation has been attributed to the presence of a small amount of magnetic impurities which contributes to the spin-flip scattering. It is therefore natural to speculate that our Cu films also have magnetic impurities. In fact, using secondary ion mass spectrometry (SIMS),[27] we observed several trace magnetic impurities (Cr, Fe, Mn, Ni, and Co) in a much thicker Cu film deposited from the same Cu source, as shown in Table I. What is unexpected, however, is that, even though we deposited Cu on CuO from the identical Cu source, we do not see the saturation of the decrease of H_2 in the Cu/CuO film.

We further observe that H_2 of the Cu/CuO film between 2 and 4 K is roughly proportional to temperature, though this is not very conclusive due to the narrow range of the measurements. Since theoretically the inelastic scattering rate by electron-electron scattering in disordered metals is also expected to roughly scale as $\sim T^1$,[28,29] this observation implies that H_2 in this sample is dominated not by the spin-flip scattering but by the inelastic scattering.

By plotting H_2 as a function of temperature in a linear scale [Fig. 3(d)] and linearly extrapolating each curve down to 0 K, the spin-flip scattering time τ_s of each sample can be estimated. We can then use the value of H_1 [Fig. 3(c)] to obtain the spin-orbit scattering time. The results of the analysis are summarized in Table II for reference. Table II clearly demonstrates that τ_s of the Cu/CuO film is anomalously long compared to that of the Cu/BI films. On the other hand, the fact that τ_{so} of each film agrees well further confirms the validity of our analysis. We note that, depending on the thickness of the films, the spin-orbit scattering times of copper films in the literature roughly range from 10^{-12} to 10^{-11} s,[19,20] which is consistent with our results. Table II also shows the results of the analysis in a slightly thicker and less disordered Cu/Al_2O_3 film for comparison. Although the data are more noisy, τ_s of this film is very similar to that of the Cu/MgO film. This observation safely excludes the possibility that the magnetic impurities originate from a surface of any particular BI substrate.

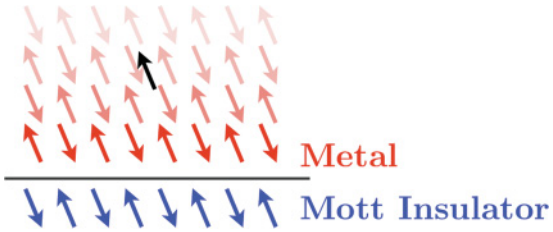

FIG. 4. (Color online) Schematic picture of the proximity effect of antiferromagnetism implied by our experimental results. The arrows represent electron spins. This figure serves as an intuitive understanding of how the electron spins inside the metal are polarized by the surface spins of the antiferromagnetic insulator, and how the spin of each magnetic impurity, which is represented as a black arrow, is quenched due to the interactions with neighboring spins in the metal. Note that the actual spatial configuration of spin density induced in the Cu is probably much more complicated than depicted in this figure due to the low symmetry of the surface spin configuration of the CuO.

All the experimental results presented so far suggest a single idea: While all the Cu films contain magnetic impurities, the spin-flip scattering by the magnetic impurities in the Cu/CuO film is suppressed due to the adjacent CuO layer. We can understand this phenomenon in the following way. Since the spins in CuO are antiferromagnetically aligned below its Néel temperature (∼200 K) as depicted in Fig. 4, each nearly free electron in the Cu is spin polarized by the superposition of Ruderman-Kittel-Kasuya-Yoshida (RKKY) interactions[31–33] from all the spins on the surface layer of the CuO,[34] which results in an AF alignment of spins inside the Cu. In this situation, the spin of each magnetic impurity feels the spin polarization of mobile electrons around it through a conventional exchange interaction. Such an interaction with polarized spins naturally creates an energy cost for the spin-flip process of the magnetic impurity. When the temperature is lower than this energy cost, the spin-flip scattering by the magnetic impurity is exponentially suppressed.

It is worthwhile to mention that the effective thickness extracted from the slope of Fig. 1 is smaller than the nominal thickness (3 nm), as shown in the Table II. This is most likely due to the oxidation of Cu by moisture in air,[36] which could heavily affect the transport properties.[20] We however

TABLE II. Summary of the magnetoconductance analysis on our films. d and R_s represent the thickness and the minimum sheet resistance, respectively. The thickness d is estimated from dR_s/dT (the slope of Fig. 1) between 150 and 200 K. Spin-orbit, inelastic, and spin-flip scattering times are evaluated using the data in Fig. 3. The error range of each value is simply estimated by the standard error of the linear regression. For the calculation of the scattering times, we adopted the following parameters for Cu: electron mass $= 9.1 \times 10^{-31}$ kg; Fermi velocity $= 1.6 \times 10^6$ m/s; and carrier density $= 8.5 \times 10^{28}$ m^{-3}.

	d (nm)	R_s (Ω/□)	τ_{so} (10^{-12} s)	$\tau_i T$ (10^{-11} s K)	τ_s (10^{-12} s)
Cu/CuO	1.3	312	1.4	2.7	$(7.1 \pm 0.4) \times 10^1$
Cu/MgO	1.4	208	1.3	2.7 ± 1.5	4.6 ± 0.8
Cu/Al_2O_3	1.5	138	2.1 ± 0.3	3.3 ± 2.8	6.1 ± 1.6

argue that, since the sheet resistance of our film is rather small compared to the quantum resistance, the transport of our film is not assumed to be very percolative, and our magnetoconductance analysis using the weak antilocalization is still valid. This argument is further supported by the observation that H_1 is correctly estimated to be temperature independent. We also note that, while the oxygen atoms may contribute to the spin-flip scattering, our main conclusion does not alter because it relies only on the comparison between the Cu/CuO and Cu/BI films.

The two copper films measured in a dilution refrigerator exhibit another characteristic feature below ∼1 K, a hysteresis of magnetoconductance. While the data are presented elsewhere, we here note that the presence of the hysteresis implies the extended relaxation time in spin glass[1] and is probably due to RKKY interactions between magnetic impurity spins inside the Cu films.[37] We emphasize that the two copper films with different substrates have similar magnitudes of hysteresis. This observation suggests that the type of magnetic impurities and their concentration are similar in both films, and is consistent with our interpretation of the results above 2 K, which was explained above.

In conclusion, through the magnetotransport study above 2 K, spin-flip scattering is found to be suppressed in Cu/CuO films, whereas the results in Cu/BI films clearly indicate the presence of magnetic impurities. We propose that the observations are indirect evidence of the proximity effect of antiferromagnetism in the metal.

Even though the effect presented in this Rapid Communication is subtle, it might find some interesting applications in the future. For example, spintronics utilizes the electron's spin and magnetic moment to affect electrical transport. A common problem in this context is the undesired relaxation of spin-polarized carriers, possibly due to magnetic impurities. Therefore, our experimental results could have implications for future spintronic experiments.

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*komun@stanford.edu

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[37]Strictly speaking, this may not be a genuine spin glass in the sense that the relaxation time is infinite, because the spin glass should not occur in a two-dimensional system from a theoretical point of view. Even so, the relaxation time can be long enough to exhibit a hysteresis in our experimental time scale.