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Rui Zhang
University of Nebraska-Lincoln, rzhang@huskers.unl.edu

Tom A. George
University of Nebraska-Lincoln

Parashu Kharel
University of Nebraska-Lincoln, pkharel2@unl.edu

Ralph Skomski
University of Nebraska-Lincoln, rskomski2@unl.edu

David J. Sellmyer
University of Nebraska-Lincoln, dsellmyer@unl.edu

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Susceptibility of Fe atoms in Cu clusters

Rui Zhang,[a)] Tom A. George, Parashu Kharel, Ralph Skomski, and D. J. Sellmyer
Department of Physics & Astronomy and Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588, USA

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By putting a Kondo system of limited dimension inside an insulating matrix, the Kondo screening cloud is confined by the size of the system. This allows us to distinguish the bulk and nano-particle behaviors of such system. We have investigated the magnetic properties of 0.3 at. % Fe-doped Cu clusters with dimensions less than 20 nm embedded in a SiO_2 matrix. The magnetic measurements are consistent with the Kondo interaction, and net antiferromagnetic Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions between several Fe atoms in one cluster are estimated to have a very small effect. To understand the low-temperature susceptibility reduction, we compare Brillouin functions with exact quantum-mechanical solutions for interacting spin-1 particles and with the Kondo predictions for confined nanoparticles. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4799617]

I. INTRODUCTION

The Kondo effect is normally associated with a low-temperature resistivity minimum in magnetically doped metals.[1] The phenomenon has been known for more than eighty years; ever since its discovery, it has become a testing ground for many numerical and analytical theories for the many-electron problem.[2] However, the investigation of the phenomenon remains experimentally challenging due to the nature of the Kondo effect. It has recently attracted renewed attention leading to new insights into the problem.[3]

The basis of the Kondo effect is scattering and screening of conduction electrons by a magnetic impurity at low temperatures. Impurity spins in non-magnetic metals surround themselves with a cloud of screening electrons, the Kondo cloud. Aside from commonly used bulk resistivity measurements, several other experimental techniques used to investigate the Kondo effect include scanning tunneling microscopy[4] and electrical measurements of quantum dots.[5] In most studies, the Kondo cloud diameter is smaller than the dimensions of the investigated systems. As our previous study shows,[3] even for nanoscale (or mesoscopic) Kondo effect studies, the conducting electrons can still travel beyond the borders of the Kondo cloud due to either the surrounding conducting matrix or the contacts required for such measurement.[6] In nanoparticles, the conduction-electron states are discrete and the number of itinerant electrons contributing to the Kondo effect becomes smaller at low temperature. This alters the Kondo behavior and reduces the low-temperature magnetic susceptibility.[3] Therefore, it is important to establish a system in which bulk and nanoscale Kondo effects can be distinguished.

The Kondo cloud can be restrained by putting magnetic impurities within an insulated metallic cluster with dimensions smaller than that of the Kondo cloud.[3] Although resistivity measurements are difficult to perform for such a system, we can investigate the Kondo effect by studying the magnetic properties of such clusters.

II. SAMPLE PREPARATION AND CHARACTERIZATION

The clusters were generated in a home-made cluster-deposition system using DC magnetron sputtering in an Ar/He environment after achieving a base pressure of 8×10^{-8} Torr.[7] A 3-in. composite target was designed to give an iron concentration of 0.3 at.% in the Cu(Fe) clusters. The gas aggregation chamber, where the clusters condensed in-flight, was cooled by liquid nitrogen. A pressure differential between the aggregation and deposition chambers drove the clusters through a 7 mm orifice and onto a substrate at ambient temperature. An insulating matrix of SiO_2 was sputtered simultaneously onto the substrate from within the deposition chamber to ensure isolation of the individual copper clusters. The substrate normal was tilted 20° from the cluster incidence and 70° from the SiO_2 particle beam for optimal co-deposition. Unless specified otherwise, cluster layers are reported in nominal thickness throughout this paper. The cluster size distribution was determined by transmission electron microscopy (TEM) from a Cu(Fe) cluster layer covered by SiO_2 deposited on a copper grid.

Magnetic measurements were performed on a sample consisting of approximately 16% volume percent of Cu(Fe) clusters in a 780 nm thick SiO_2 matrix on a Kapton film substrate. The 1 in. square flexible substrate was then folded into a hollow cylinder of 3 mm height and 5 mm diameter for measurement in a superconducting quantum interference device (SQUID) magnetometer. The zero field cool (ZFC) measurement covered the temperature range of 2 K to 150 K with an applied field of 200 Oe. For comparison, a thin film sample of 50 nm of the same Cu(Fe) was sputtered on a Si substrate. The resistivity of that sample was measured from 2 K to 300 K with a Physical Property Measurement System (PPMS) to estimate the Kondo temperature of an analogous bulk system.

III. RESULTS AND DISCUSSION

The film sample prepared for resistivity measurement shows clear Kondo behavior as shown in Fig. 1. As temperature

[a)]Author to whom correspondence should be addressed. Electronic mail: rzhang@huskers.unl.edu

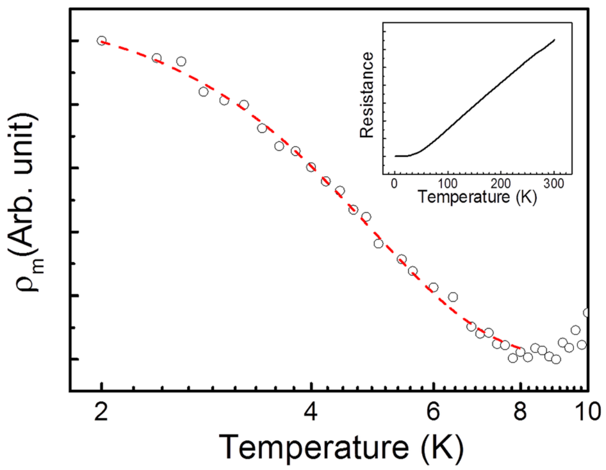

FIG. 1. Temperature dependence of resistivity of the film sample $\rho_m = \rho - \rho_{min}$ between 2 K and 11 K. The dashed line represents the NRG fitting. The inset shows resistivity as a function of temperature measured between 2 K and 300 K.

decreases from 300 K, the resistivity drops linearly with the decreasing temperature. However, a resistivity minimum followed by a logarithmic temperature dependence is observed below 10 K. As the temperature decreases further, the resistivity shows a tendency towards saturation. The measured result was fitted using the numerical renormalization-group (NRG)-like equation[8]

$$\rho_m = \rho_0 \left[1 + \left(2^{\frac{1}{\alpha_s}} - 1 \right) \left(\frac{T}{T_K} \right)^{\xi_s} \right]^{-\alpha_s}, \quad (1)$$

where ρ_0 is the residual resistivity, T_K is the Kondo temperature, and ξ_s and α_s are fitting parameters.[9] As shown in Fig. 1, a reasonably good fit can be achieved using the above equation and the T_K acquired from the fit is 4.2 K. The Kondo screening length ξ_K can be estimated using the following equation:[10]

$$\xi_K = \frac{\hbar v_F}{k_B T_K},$$

where $v_F = 1.57 \times 10^6$ m/s is the Fermi velocity of copper.[11] Therefore, the estimated Kondo screening length is around 3 μm. As revealed by the TEM image in Fig. 2, the Cu(Fe) clusters have an average diameter of around 4 nm, which is much smaller than the estimated Kondo-cloud screening length. The ZFC measurement for Cu(Fe) clusters embedded in a SiO_2 matrix is shown in Fig. 3. The curve shows clear paramagnetic-like behavior and no downturn was observed above 2 K. It can be fitted reasonably well with the following expression:

$$M = \chi_0 H + \frac{CH}{T - \theta},$$

where χ_0 represents the temperature-independent term, while the second term is due to the impurities plus Kondo interactions. The fitting yields $\theta = -0.7$ K, which is smaller than the value acquired in bulk system,[12] suggesting the Kondo interaction is suppressed by the reduced size of the system. The inset of Fig. 3 shows the $M(H)$ curve after subtracting

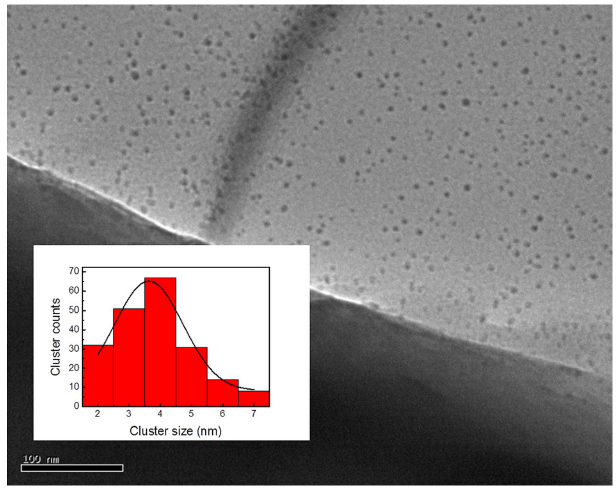

FIG. 2. TEM image of Cu(Fe) clusters deposited on TEM grid. The inset is the cluster size distribution measured from the sample.

the diamagnetic background, and a reasonable fit can be achieved using the Brillouin function with $S = 1$.

Since the Fe atoms are randomly distributed in the Cu matrix, they are likely to experience coupling due to RKKY interactions. If these interactions are predominantly antiferromagnetic (AFM), then they may mimic or mask the Kondo effect, because both mechanisms reduce the low-temperature susceptibility with respect to the Curie $1/T$ law. The interaction effect must be treated quantum-mechanically, because the Kondo effect consists in the discrete flipping of individual spins, and such a quantum-mechanical flipping can also be caused by AFM interactions. A classical interaction would yield an unphysical continuous "wiggling" of the coupled spins and blur the discrete character of the Kondo effect.

For interacting spin-1 particles, the spin-1/2 Pauli matrices must be replaced by the spin operators[13]

$$S_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \quad S_y = \frac{i}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix};$$
$$S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \quad (2)$$

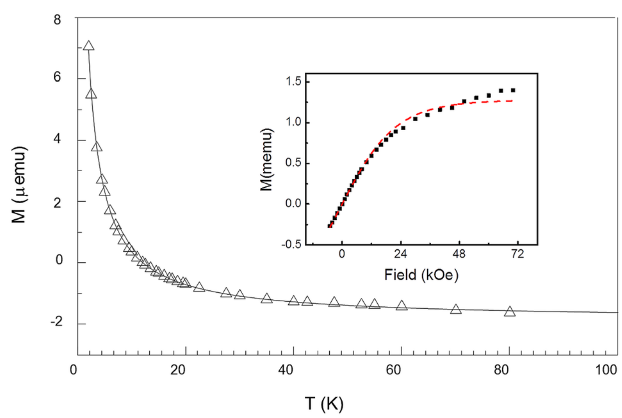

FIG. 3. ZFC measurement of Cu(Fe) clusters embedded in a SiO_2 matrix. The solid line is the fit to the data. The inset is the M vs. H curve measured at 2 K and the dashed line is the Brillouin function fit to the data.

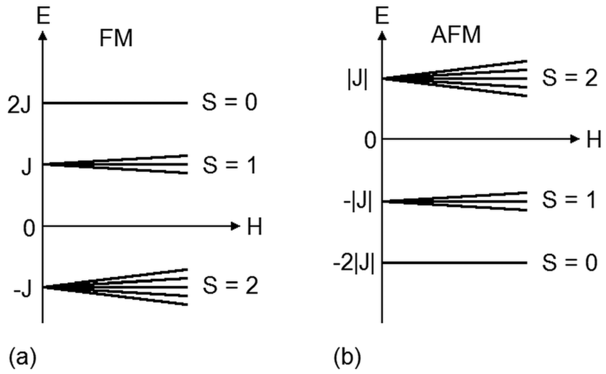

FIG. 4. Energy levels for two interacting $S=1$ atoms with (a) ferromagnetic and (b) AFM RKKY interaction.

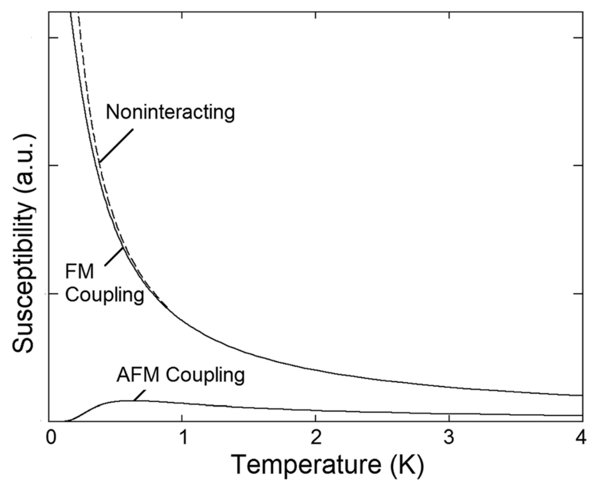

FIG. 5. Susceptibility of non-interacting and interacting Fe atoms in Cu. Only pairs of Fe atoms interacting by positive or negative RKKY interactions are considered, and the susceptibility of the non-interacting system has been normalized to agree with the high-temperature part of the FM curve.

For isolated Fe particles in a field $\mathbf{H} = H\,\mathbf{e}_z$, only the last matrix is important, and the susceptibility is given by the Brillouin function $B_1(x)$ where $x = g\mu_B S/k_B T$, $S=1$. We consider pairs of $S=1$ spins S_1 and S_2, coupled by Heisenberg exchange $-J\ S_1{\cdot}S_2$. The interactions can then be written as direct products of the matrices of Eq. (2) for S_1 and S_2. The diagonalization of the resulting 9×9 matrix yields an $S=2$ quintuplet of energy $-J$, an $S=1$ triplet of energy $+J$, and an $S=0$ singlet of energy $+2J$. Fig. 4 shows these levels for positive (ferromagnetic (FM)) and negative (AFM) values of J.

In the ferromagnetic case, the main contribution to the susceptibility comes from the ferromagnetic quintuplet, bottom of Fig. 4(a), with small corrections due to the triplet. For antiferromagnetic coupling, the situation is more complicated. The AFM ground state ($S=0$) does not contribute to the susceptibility, but the $S=1$ triplet is fairly close to the singlet and gives rise to a Van-Vleck-type susceptibility. Physically, the singlet and triplet states mean that the two coupled spin-1 atoms involve four spin-1/2 electrons with "two spins up, two spins down" (singlet) and "three spins up, one spin down" (triplet), and the corresponding wave functions are obtained by diagonalizing the above-mentioned 9×9 matrix.

The susceptibilities are readily obtained via the partition functions belonging to Figs. 4(a) and 4(b). In the FM case (a), the result is, in lowest order, equal to the susceptibility predicted by the Brillouin function $B_2(x')$ where $x' = g\mu_B 2S/k_B T$, $S=1$. In the AFM case (b), the lowest-order susceptibility is zero, but there is a small Van-Vleck contribution proportional to the small parameter $\lambda = \exp(-|J|/k_B T)$. By contrast, the triplet correction to the FM quintuplet is of the order $\lambda^2 = \exp(-2|J|/k_B T)$. Fig. 5 compares the corresponding susceptibility contributions. In the present case, the average Fe-Fe distance is 1.6 nm. Around this distance, the RKKY exchange is negative and small, less than about 0.5 K in temperature units, or positive,[14] and should not interfere very much with the Kondo effect.

IV. SUMMARY

In conclusion, we have observed the Kondo effect in dilute Cu:Fe thin-film samples. Our magnetic susceptibility measurements indicate that the effect is reduced in isolated Cu:Fe particles. This is ascribed to the strong reduction of the Kondo screening cloud, which cannot be bigger than the particle size, and consistent with theoretical predictions. RKKY interactions between Fe atoms in one cluster are estimated to yield very small corrections.

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