Size effects on the local magnetism and Kondo behavior of isolated Fe impurities in nanocrystalline metallic hosts

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(Received 16 July 2004; published 30 March 2005)

Measurements of the local susceptibility and 3*d* spin relaxation rate of single Fe impurities embedded in Cu and Ag nanoparticles indicate a strong influence of lattice size on the magnetism and Kondo temperature, T_K. With a reduction in particle size, T_K increases in nanocrystalline Ag, but decreases in nanocrystalline Cu. Supported by macroscopic host susceptibility data that indicate enhanced Pauli paramagnetism for Cu nanoparticles, we suggest that size-induced host spin polarization stronglyinfluences the Kondo behavior.

DOI: 10.1103/PhysRevB.71.094429 PACS number(s): 75.20.Hr, 73.22.−f, 75.75.+a, 76.80.+y

Local magnetism of 3*d* impurities in nonmagnetic metallic hosts is a subject of intense experimental and theoretical investigations. A key problem is the study of Kondo effect arising from antiferromagnetic exchange interaction between the impurity moment and host-conduction electrons leading to moment instability below a characteristic temperature T_K. While extensive studies have been carried out for many *d* and *f* impurities in bulk metallic hosts[1,2] little information is available on the Kondo behavior of single magnetic impurities in nanocrystalline materials. Recently resistivity studies in thin films and nanowires of Au(Fe), Cu(Cr), and Cu(Fe) alloys have revealed the suppression of Kondo interaction below a critical thickness and width.[3] The results, initially interpreted as being due to confinement of the Kondo screened electron cloud, were later shown to arise from size-induced magnetic anisotropy effects.[4]

Nanocrystalline materials have recently attracted considerable attention due to their novel physicochemical properties and practical applications. Since the energy bands of a bulk solid split into discrete levels with a reduction in size,[5] physical properties of nanoparticles show marked differences from those of bulk materials. Size dependent changes in structural, electronic, and magnetic properties have been observed in many metals.[5] In this context, one can ask: Does finite host lattice size affect single impurity local magnetism? If so, how does it influence spin fluctuation and Kondo interaction? We approach this problem by studying the local magnetism and 3*d* spin dynamics of isolated Fe impurities in nanocrystalline Cuand Ag hosts using the γ-ray perturbed angular distribution (TDPAD) technique. Fe in noble metal hosts is a typical local moment system for which T_K values have been measured accurately.[1,2,6] By comparing the magnetic behavior of Fe in bulk and nanocrystalline noble metals, we can obtain crucial information on finite size effects on local moments and Kondo interaction. Preliminary results for Fe in Ag-nanoparticles have been reported earlier.[7]

In this Brief Report we show that the local susceptibility and 3*d* spin dynamics of ^{54}Fe implanted in nanocrystalline Cu and Ag reveal a strong influence of particle size on the magnetic moment of Fe, particularly on the Kondo temperature T_K. While size reduction in Ag leads to enhancement of T_K, data on Cu nanoparticles indicate a drastic suppression of the Kondo interaction. With the help of macroscopic susceptibility data for the host matrix, which reflects an enhanced Pauli paramagnetism for nanocrystalline Cu, we show that the sign and strength of the size-induced spin polarization of host conduction band electrons play an important role on the magnetism and Kondo behavior of Fe in nanocrystalline materials.

The TDPAD experiments were carried out at the Pelletron Accelerator Facility at TIFR. The magnetic response of Fe atoms in the hosts of interest was studied via hyperfine interaction of the 10^+ isomeric state of the ^{54}Fe nucleus ($T_{1/2}$ = 360 ns, g_N = 0.728) produced by the reaction ^{45}Sc(^{12}C, $p2n$)^{54}Fe. The recoiling ^{54}Fe nuclei were implanted deep ($\sim$1 to 2 μm) inside the host matrix at concentrations well below 1 ppm. Measurements were performed within a time window of 10 ns to 2 μs immediately after implantation. These experimental conditions ensure negligible impurity-impurity interaction and the results reflect the magnetic response of a truly isolated impurity. Observations were made in the temperature range of 17–300 K and applied magnetic field of 2 T using γ-ray detectors placed at ±45° with respect to the beam direction. Further details on the TDPAD method can be found in Ref. 8.

Nanocrystalline samples of Cu and Ag were prepared by dc magnetron sputtering from a target of 99.99% pure metal onto thin (0.05 mm) Al or Cu substrates cooled to $\sim$100 K. The sputtering was carried out in flowing argon at a pressure of $\sim$100–200 mTorr. The deposition thickness was $\sim$5 mg/cm^2. We also prepared a thin disk of the nanocrystalline sample by scraping and mildly pressing the sputter-deposited particles. The samples were characterized by x-ray diffraction and electron microscopy. Details of nanoparticle synthesis and characterization are available in Ref. 9. The mean crystallographic domain size "*d*" was calculated from the instrument-corrected Scherrer broadening of the [111] reflection of Cu/Ag using the formula $d = 0.94\lambda / B \cos\theta$.[10] The virgin (unpressed) nanocrystalline films had an average crystallite size of 7(2) and 30(4)nm for Cu and 19(2)nm for Ag while the particle size for the pellets was $\sim$20 nm. The lattice constants of the nanocrystalline samples were close to the bulk values within ±0.25%.

Figure 1 shows typical spin rotation spectra,[8] $R(t)$, and their Fourier transforms for ^{54}Fe in bulk and nanocrystalline Cu and Ag hosts. All the spectra exhibit a single frequency

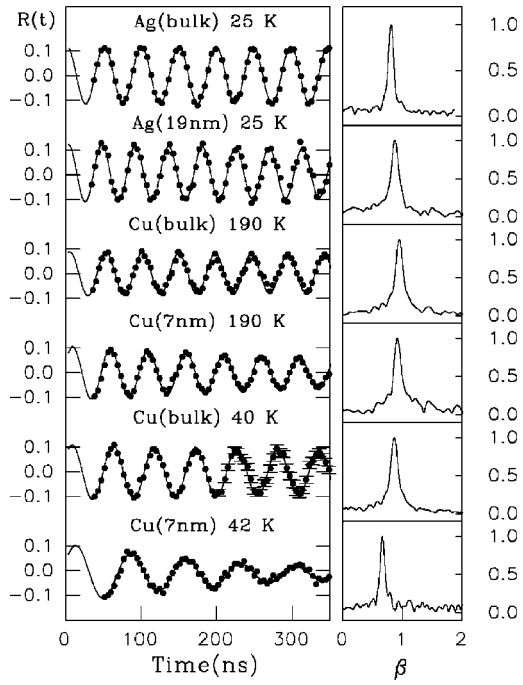

FIG. 1. Spin rotation spectra, $R(t)$ (left panel) and their Fourier transforms (right panel) for ^{54}Fe in bulk and nanocrystalline Cu and Ag hosts.

with high anisotropy suggesting that the implanted Fe atoms occupy a well-defined lattice site that is likely to be substitutional. The narrow frequency distribution also indicates that a large majority of the Fe atoms are embedded within the nanoparticles rather than in the grain boundaries. The spectra were fitted to the function:[8] $R(t) = (3/4)A_{22}\exp(-t/\tau_N)\sin[2(\omega_L t - \phi)]$ to extract the Larmor frequency ω_L and the nuclear relaxation time τ_N. The local susceptibility of Fe, $\chi_{loc} \equiv \beta - 1$ calculated from[2,8] $\omega_L = \hbar^{-1} g_N \mu_N B_{ext} \times \beta$ is shown in Fig. 2. In both bulk and nanocrystalline samples, χ_{loc} shows a strong temperature dependence, which indicates a large local moment for Fe.

To examine the effect of lattice size on the local magnetism of Fe, we now compare the $\beta(T)$ in nanocrystalline and bulk hosts. The data (Fig. 2) clearly show that the magnetic

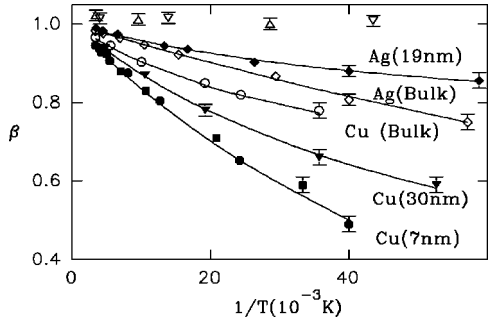

FIG. 2. Local susceptibility $\beta(T)$ of Fe in bulk (open symbols) and nanocrystalline (closed symbols) Cu and Ag as a function of $1/T$. The solid lines correspond to fits by Curie-Weiss law: $\beta(T) - 1 = C/(T + T_K)$. The data for Fe in CuO (△) and Cu_2O (∇) indicate nonmagnetic behavior.

TABLE I. Summary of Curie constant, Kondo temperature T_K, and magnetic moment μ_{Fe} for Fe in bulk and nanocrystalline Cu and Ag.

Host	Curie constant C (K)	T_K (K)	μ_{Fe} (μ_B)
Cu(bulk)	−11.0(10)	25.5(15)	2.92
Cu(nano:7 nm)	−17.5(10)	8.5(15)	5.82
			3.59[a]
Cu(nano:30 nm)	−14.9(10)	16.6(15)	4.66
Ag(bulk)	−5.2(5)	2.3(8)	3.05
Ag(nano:19 nm)	−5.0(10)	17.2(8)	2.86

[a]Fe moment estimated using the maximum value of $B(0) = -14$ T (Ref. 11).

properties of Fe embedded in nanocrystalline metals differ significantly from that in the corresponding bulk metal. Further, the size-induced change in $\beta(T)$ relative to bulk hosts is different for Cu and Ag. While $\chi_{loc}(T)$ is reduced in nano-Ag, it shows a substantial increase in nano-Cu. The $\beta(T)$ could be fitted to the Curie-Weiss law: $\beta - 1 = C/(T + T_K)$ where the Curie constant $C = g\mu_B(S+1)B(0)/3k_B$ provides a measure of the Fe magnetic moment $\mu_{Fe} = gS$ and T_K is the Kondo temperature. Here, $B(0)$ is the magnetic hyperfine field at $T = 0$ K and $S = S_{imp} + S_{host}$ is the net spin due to the impurity atom (S_{imp}) and possible spin polarization of host conduction electrons (S_{host}). The derived values for C and T_K are summarized in Table I. The μ_{Fe} estimated using $B(0) = -46$ kG for Ag and $B(0) = -100$ kG for Cu Refs. 11 and 12 are shown in Table I. For Fe in bulk Cu and Ag the magnetic moment $\mu_{Fe} \sim 3\mu_B$ corresponds to impurity spin $S_{Fe} = 3/2$ which agrees with earlier results.[11–13] In nano-Ag, the μ_{Fe} is slightly smaller than its value in the bulk metal. These results suggest that the host spin polarization in bulk Cu and Ag is negligible, and that the S_{host} for Fe in nano-Ag is small and negative. In contrast, the Curie constant observed for nano-Cu yields $\mu_{Fe} = 5.82\mu_B$ for 7 nm and $4.66\mu_B$ for 30 nm. Taking $B(0)$ to be as high as −140 kG,[14] the Fe moment in nano-Cu (7 nm) comes out to be $3.59\mu_B$ which is still much larger than the value of $\mu_{Fe} = 2.9\mu_B$ in bulk Cu. This clearly indicates a large ferromagnetic spin polarization (S_{host}) for nano-Cu. We point out that measurements in CuO and Cu_2O show nonmagnetic behavior of Fe with $\beta \sim 1.0$ which assures us that the results observed in the nanocrystalline samples cannot be ascribed to extrinsic impurities but are genuine lattice size effects.

Figure 3 shows the temperature dependence of the macroscopic magnetic susceptibility (χ) of the unimplanted bulk and nanoparticle samples measured using a superconducting quantum interference device magnetometer. Clearly, the nanocrystalline metals show a much higher susceptibility than their bulk counterparts. In particular, nano-Cu shows a strongly enhanced, Pauli-type susceptibility with a magnitude comparable to that for exchange enhanced metals such as Pd and Pt.[1] Since $\chi_P \sim \mu_B^2 \rho(E_F)$, the nano-Cu data imply a high density of states at the Fermi energy, $\rho(E_F) \sim 1.7$ states/eV atom, probably due to a large contribution from the Cu d-band electrons which move closer to the

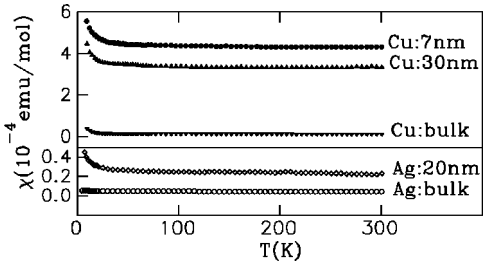

FIG. 3. Temperature dependence of macroscopic susceptibility for unimplanted bulk and nanocrystalline Cu and Ag.

Fermi level with decreasing particle size. Note that Fe in Pd and Pt is known to cause strong ferromagnetic spin polarization of host *d*-band electrons.[6,15] It is therefore not surprising that Fe in nanocrystalline Cu induces a similar effect. In nano-Ag, the incremental susceptibility $\delta\chi=\chi_{nano}-\chi_{\text{bulk}}\sim 2\times 10^{-5}$ emu/mol is much smaller than in Cu. Since the 4*d* band in Ag metal is located ~4 eV below E_F,[16] a small shift in its position due to size reduction does not contribute much to the $\rho(E_F)$. The χ data in this case is consistent with a slight increase in $\rho(E_F)$ mainly due to *s*-electrons. This also explains the weak negative host polarization observed in the $\beta(T)$. We will show that the spin polarization of host conduction electrons plays a crucial role in the Kondo behavior of Fe.

Next we discuss the spin fluctuation of Fe in nanocrystalline Cu and Ag hosts which scales with the Kondo temperature T_K obtained from the Curie-Weiss fitting of the local susceptibility data. The $\beta(T)$ response of Fe in nano-Ag yields a Kondo temperature $T_K\sim 17$ K which is substantially higher than the value $T_K=2$ K observed in bulk Ag. On the other hand, compared to $T_K\sim 26$ K for Fe in bulk Cu, the $\beta(T)$ data in nano-Cu yields a significantly smaller T_K (~8 K for 7 nm) concomitant to the substantial increase of the Curie constant ($C=-17.5$ K) discussed earlier. The high T_K of Fe in nano-Ag suggests a large enhancement of the Fe-3*d* spin fluctuation rate, τ_J^{-1}. In contrast, our data for nano-Cu indicate a drastic suppression in τ_J^{-1}. A reduction of τ_J^{-1} in nano-Cu is also visible from the τ_N data shown in Fig. 4. Compared to bulk Cu, the strongly damped $R(t)$ spectra in nano-Cu reflects a significantly lower value of τ_N which in turn implies a sharp reduction of τ_J^{-1} Ref. 17 that exhibits a Korringa-like temperature dependence ($\tau_N\propto\tau_J^{-1}\propto T$).

What is the physical reason for the suppression of the

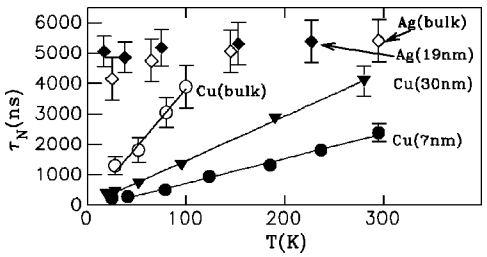

FIG. 4. Nuclear relaxation time τ_N as a function of temperature for ^{54}Fe in bulk (open symbols) and nanocrystalline (closed symbols) Cu and Ag. The linear dependence of τ_N with T (solid lines) is indicative of the Korringa-like relaxation process.

Kondo interaction in nano-Cu while there is a large increase of T_K in nano-Ag? The Kondo temperature of Fe expressed as[18] $T_K\sim T_F\exp\{-1/[J\rho(E_F)]\}$ can increase or decrease, depending on the magnitude of the effective antiferromagnetic exchange interaction $J\rho(E_F)$ between Fe-3*d* and host conduction electrons. Here, $J\sim -V_{kd}^2/\epsilon_d$ is the exchange constant which depends on the hybridization strength V_{kd} and the position of the Fe-3*d* level (ϵ_d) with respect to the Fermi energy E_F, and $\rho(E_F)$ is the density of states (DOS) at E_F. As discussed earlier, the DOS for the nanocrystalline samples is larger than their bulk values.[16] Assuming the Fe-3*d* level to be pinned near E_F due to a higher DOS and the consequent increase in the *s*-*d* exchange interaction, the T_K of Fe in the nanocrystalline samples is expected to be larger than its corresponding bulk value. The observed magnetic behavior of Fe in nano-Ag with $T_K=17$ K is consistent with such a model. The higher T_K of Fe in nano-Ag is also supported by recent Mössbauer data.[19] An increase in T_K has also been reported for Ce in nanosized (Ce,Al) alloys.[20] Extrapolating this trend and assuming J to be antiferromagnetic, one expects Fe in nano-Cu to be nonmagnetic with $T_K\gg 10^3$ K. Instead, the T_K for Fe in 7 nm-Cu turns out to be ~8 K, suggesting a sharp decrease in the effective exchange interaction strength $J\rho(E_F)$. This is confirmed from our spin relaxation data (Fig. 4). Using $\tau_J^{-1}=4\pi\hbar^{-1}[J\rho(E_F)]^2k_BT$,[18] the data yield $J\rho(E_F)\sim 0.06$ for nano-Cu as compared to ~0.11 in the bulk metal. From the trend of Fe magnetism in bulk and nanocrystalline materials, particularly the observation of large S_{host} and the concomitant decrease of T_K in nano-Cu, we believe that the induced spin polarization of the host conduction band electrons leading to a ferromagnetic coupling with the Fe moment can effectively reduce $J\rho(E_F)$ and result in lower spin fluctuation and dimished T_K. The suppression of Kondo interaction observed for Fe in nano-Cu is consistent with the basic features of the results of thin films and nanowires,[3] though the disagreement with respect to the size dependence of T_K needs to be investigated further.

The magnetic behavior of Fe in nanocrystalline Cu shows a striking similarity with that of 3*d* impurities in exchange-enhanced *d*-band metals such as Pd and Pt, in which the ferromagnetic spin polarization of the host *d*-band electrons leads to giant moments with extremely small T_K.[2] Suppression of the Kondo temperature due to ferromagnetic host spin polarization is also observed for 4*d* impurities in different metallic hosts.[21,23] It is quite plausible that the ferromagnetic spin polarization causes a strong interatomic interaction between the impurity and host conduction electrons and competes with the usual antiferromagnetic exchange interaction, thereby successfully suppressing spin fluctuation and diminishing T_K. This model is also consistent with recent theoretical calculations,[22] which predict that the ferromagnetic interaction between the impurity and host conduction electrons drastically reduces the Kondo resonance near E_F.

In conclusion, we have studied the local magnetism and Kondo behavior of isolated Fe impurities in nanocrystalline noble metals by the TDPAD method. A comparison of the local susceptibility and 3*d* spin dynamics of Fe in nanocrystalline Cu and Ag with similar data from the respective bulk metals reveals a strong influence of particle size on the Fe

magnetism, and especially the Kondo temperature, T_K. While the magnetism of Fe in nano-Ag, with a high T_K, is consistent with enhanced antiferromagnetic *s-d* interaction, we have shown that the magnetism and Kondo temperature of Fe in nano-Cu are strongly influenced by the ferromagnetic spin polarization of the conduction band electrons of the host. The interpretation of our results provide an important basis for the understanding of Kondo interaction of magnetic impurities in metallic hosts including nanocystalline materials. This also illustrates the important common role of ferromagnetic host spin polarization on the spin fluctuation and the Kondo behavior of 3*d* and 4*d* magnetic impurities in bulk metals as well as nanosized solids.

We thank S. M. Davane and N. Kulkarni for help during the experiments and the Pelletron accelerator staff for their cooperation.

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