Lattice Size Induced Moment Formation on Isolated Fe Atoms in Nanocrystalline Nb

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Measurements of the local susceptibility and 3*d* spin relaxation rate for single Fe impurities embedded in a nanocrystalline Nb host indicates the emergence of a local moment on Fe at and below a critical size of 11 nm. Our *ab initio* electronic structure calculations show that the moment formation occurs due to Stoner enhancement arising from a size dependent lattice expansion and a consequent shift in the Fermi level. We also show that a size-induced positive host spin polarization of the Nb-4*d* band electrons strongly influences the fluctuation rate of the Fe moment.

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The formation of local moments on isolated 3*d* impurity atoms embedded in nonmagnetic metallic hosts has been a subject of intense experimental and theoretical investigations. Studies have been carried out on several 3*d*, 4*d*, and 4*f* impurities in a variety of bulk metallic hosts [1–4] but very little is known about the local magnetism of single impurity atoms in *nanocrystalline* metals. Since quantum size effects [5] lead to marked deviations in the structural, electronic, transport, and magnetic properties of metallic nanoparticles from those of bulk materials, it would be pertinent to study the effect of the size of the host matrix on the local magnetism of an isolated impurity atom. This raises two important questions: (i) Can a reduction in the size of the host lattice lead to the formation of a local moment on an impurity atom, and (ii) will such a moment be stable against spin fluctuations? Local moment formation is governed by the condition $IN_l(E_F) \geq 1$, where I is the Stoner exchange parameter and $N_l(E_F)$ is the impurity local density of states at the Fermi energy, E_F [6]. The stability of the moment depends on the spin fluctuations caused by Kondo interaction between the impurity-*d* and the conduction electrons. Finite size effects on the Kondo interaction have been reported from resistivity measurements in thin films and nanowires of some dilute magnetic alloys [7]. More recently, γ-ray time differential perturbed angular distribution (TDPAD) studies of isolated Fe impurities in Cu and Ag nanoparticles revealed a strong influence of the particle size on the magnetism of Fe, and especially on the Kondo temperature T_K [8]. However, whether lattice size itself can induce moment formation on an impurity atom remains an open question.

We address this problem via a TDPAD study of the local magnetism of isolated Fe atoms in a nanocrystalline Nb (nano-Nb) host, backed by *ab initio* electronic structure calculations using density functional theory (DFT). Note that an Fe impurity in bulk Nb is known to be *nonmagnetic* [2]. DFT calculations also show that the local density of states (LDOS) of Fe in bulk Nb does not satisfy the Stoner condition for local moment formation [6]. Recent investigations in nano-Nb show that the unit cell volume increases with decreasing particle size [9], which may reduce the hybridization between the Fe-3*d* and host-conduction band electrons, and hence promote the formation of a local moment. Similarly, a size-induced narrowing of the energy bands may increase the DOS at E_F, resulting in the Stoner condition being satisfied, and thus favor local moment formation.

Here, we report the emergence of a local moment on Fe impurity atoms embedded in nano-Nb from a study of local susceptibility and 3*d* spin dynamics by TDPAD measurements. Whereas Fe in bulk Nb is nonmagnetic, Fe atoms in nano-Nb exhibit Curie-Weiss type local susceptibility for particle sizes ≤ 11 nm, indicating local moment formation with a low T_K. *Ab initio* electronic structure calculations confirm that the Stoner enhancement arising from a size dependent tuning of the Fermi level leads to moment formation at and below a critical size of 11 nm. We suggest that a size-induced positive host spin polarization of Nb-4*d* band electrons strongly influences the spin fluctuation rate of the Fe moment.

The TDPAD experiments (see Ref. [10] for details) were carried out at the Pelletron Accelerator Facility at TIFR. The magnetic response of Fe atoms in the host 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 (≈ 1 μm) inside the host matrix at concentrations well below 1 ppm [11]. 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 15–300 K and applied magnetic field of 2 T using γ-ray detectors placed at $\pm 45°$ and $\pm 135°$ with respect to the beam direction.

Nano-Nb thin films (≈ 2 μm thick) were deposited on Si substrates by dc magnetron sputtering from a 99.99% pure Nb target. The mean crystallographic domain size (d_{XRD}) was calculated from the instrument-corrected

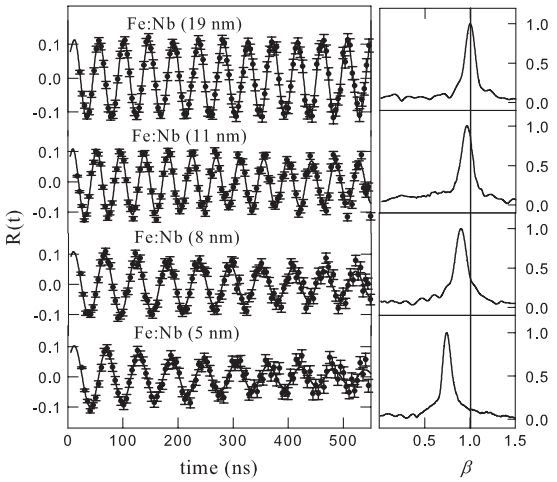

FIG. 1. Spin rotation spectra, $R(t)$ recorded at 15 K (left panel) and their Fourier transforms (right panel) for ^{54}Fe in nanocrystalline Nb with varying d_{XRD}.

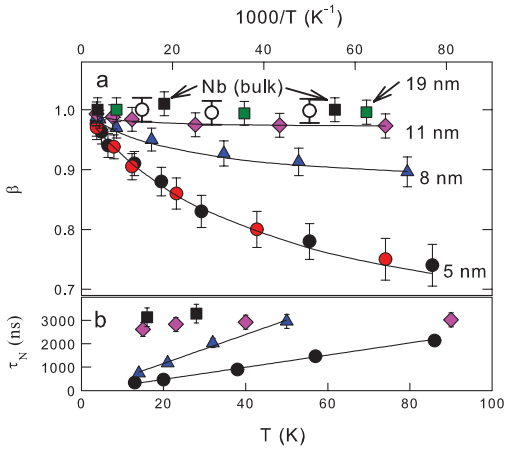

FIG. 2 (color). Temperature dependence of: (a) the local susceptibility $\beta(T)$ and (b) nuclear relaxation time τ_N of ^{54}Fe in bulk and nano-Nb. Red and black circles are data taken for two different samples with $d_{\mathrm{XRD}} = 5$ nm. Open circles correspond to $\beta(T)$ of Fe in Si substrate. Solid lines show fits to the Curie-Weiss law. The linear dependence of τ_N on T indicates a Korringa-like relaxation.

broadening of the [110] x-ray reflection of Nb using the Scherrer formula [12]. Samples with different mean sizes were obtained by controlling the sputtering gas (Ar) pressure and applied power [13]. We studied a number of samples with d_{XRD} in the range 5–20 nm and a size distribution $\leq 20\%$, as determined by x-ray diffraction line profile analysis and transmission electron microscopy. The lattice constants of the samples were found to increase from 3.30 Å for bulk Nb to 3.513 Å for nano-Nb with $d_{\mathrm{XRD}} = 5$ nm.

Figure 1 shows the typical spin rotation spectra [10], $R(t)$, and their Fourier transforms for ^{54}Fe in different nano-Nb hosts. The spectra exhibit a single frequency with high anisotropy, suggesting that the implanted Fe atoms come to rest at well-defined, probably substitutional, lattice sites. The narrow frequency distribution also indicates that most of the Fe atoms are located within the nanoparticles rather than at the grain boundaries. The spectra were fitted to the function [10] $R(t) = (3/4)A_{22}e^{-t/\tau_N}\sin[2(\omega_L t - \phi)]$ to extract the Larmor frequency ω_L and the nuclear relaxation time τ_N. Figure 2 shows the local susceptibility of Fe, $\chi_{\mathrm{loc}}(\equiv \beta - 1)$, estimated from [2,10] $\omega_L = (g_N \mu_N B_{\mathrm{ext}}/\hbar)\beta$ where, β is the paramagnetic enhancement factor. The nonmagnetic nature of Fe in bulk Nb [2] is confirmed by the temperature independence of the susceptibility ($\beta(T) \approx 1$). In nano-Nb, Fe is nonmagnetic for $d_{\mathrm{XRD}} \geq 19$ nm. However, on reducing the size to 11 nm and below, $\beta(T)$ shows a strong temperature dependence with values <1, indicating the presence of a local spin magnetic moment on Fe with negligible orbital contribution. Note that measurements for Fe in Si show nonmagnetic behavior with $\beta(T) = 1$ (Fig. 2). This, together with the Monte Carlo simulations [11], assures us that the ^{54}Fe atoms stop within the nano-Nb films.

The measured $\chi_{\mathrm{loc}}(T)$ data could be fitted to the Curie-Weiss law $\chi_{\mathrm{loc}}(T) = C/(T + T_K)$, where the Curie constant $C = g\mu_B(S+1)B(0)/3k_B$ provides a measure of the Fe magnetic moment, $\mu_{\mathrm{Fe}} = gS$. Here T_K is the Kondo temperature, $B(0)$ is the magnetic hyperfine field at $T = 0$ and S is the effective spin on Fe. The derived values of C and T_K are summarized in Table I. Note that a reduction in the size causes an increase in C but a decrease in T_K. The magnetic moments, μ_{Fe}, of Fe in nano-Nb were

TABLE I. Curie constant C, Kondo temperature T_K, and magnetic moment $\mu_{\mathrm{Fe}}^{\mathrm{exp}}$ of Fe in nanocrystalline Nb obtained from TDPAD. The Fe moments ($\mu_{\mathrm{Fe}}^{\mathrm{cal}}$) and hyperfine fields ($B_{hf}^{\mathrm{cal}}$) are obtained from *ab initio* calculations. m_1, m_2 and m_3 are the induced moments on the host Nb atoms in the three nearest neighbor shells around the Fe atom.

d_{XRD}	C	T_K	$\mu_{\mathrm{Fe}}^{\mathrm{exp}}$	μ^{cal}	B_{hf}^{cal}	m_1	m_2	m_3
(nm)	(K)	(K)	(μ_B)	(μ_B)	(kG)	μ_B	μ_B	μ_B
Bulk	0	⋯	0					
19	0	⋯	0					
11	−2.4(6)	119(25)	0.6(5)	0.46	−41	0.02	−0.015	−0.002
8	−6.3(5)	67(10)	1.5(3)	1.13	−79	0.05	−0.03	−0.005
5	−11.6(3)	31(5)	2.6(2)	2.14	−112	0.10	−0.05	−0.01

estimated (see Table I) using the values of $B(0)$ obtained from *ab initio* calculations, discussed below. Our data clearly indicate that the local moment that appears on isolated Fe atoms in nano-Nb, increases with reducing size (≤ 11 nm) and there is a concomitant suppression of spin fluctuations, which scales with T_K.

The size dependent reduction of T_K in nano-Nb is also reflected in the $3d$ spin relaxation rate, τ_J^{-1} of Fe which were extracted from the τ_N data [14] [Fig. 2(b)]. While the relaxation times for bulk Nb and the larger nanoparticles (≥ 11 nm) are long and temperature independent, the τ_N for the 5 and 8 nm samples are much smaller and showed Korringa type dependence: ($\tau_N \propto T$). Using the relations [15] $\tau_J^{-1}(\propto \tau_N) = 4\pi\hbar^{-1}(J\rho)^2 k_B T$ and $T_K = T_F e^{-1/J\rho}$, we obtain $T_K = 26$ K and 53 K for the 5 and 8 nm samples, respectively, which agree with the values extracted from the $\chi_{\rm loc}(T)$ data (Table I).

The experimental results were complimented by *ab initio* electronic structure calculations within the framework of density functional theory (DFT) [16,17] using a 54-atom supercell (53Nb + 1Fe) constructed with 27 units ($3 \times 3 \times 3$) of bcc Nb with experimentally observed lattice constants for the nanoparticles [13] as the only variable. Figure 3 displays the local density of states (LDOS) for the Fe impurity obtained from unpolarized and spin polarized calculations. We first consider the results from the nonmagnetic calculations and examine the Stoner condition for moment formation. Taking the Stoner exchange parameter $I = 0.925$ eV for Fe [6], we find that a local moment can exist only when $N_{\rm Fe}(E_F) \geq 1.08$ states/eV-atom. The LDOS results (Fig. 3) show that the occupied $3d - t_{2g}$ states of Fe in the bulk Nb host, strongly overlapping with the Nb-4d band, are piled up near -1.5 eV, while the empty $d - e_g$ states are pushed above E_F. As a result the DOS for Fe at the Fermi energy turns out to be rather small, $N_{\rm Fe}(E_F) \approx 0.8$ states/eV-atom, consistent with earlier results [6]. In the case of nano-Nb, the Fe LDOS does not change appreciably down to 19 nm (Fig. 3). Since $N_{\rm Fe}(E_F)$ is less than the Stoner limit, the Fe atoms are expected to be nonmagnetic in nano-Nb down to a size 19 nm, in agreement with our experimental results. With a further reduction in size, the Fermi level shifts to lower energy, resulting in a shift of the Fe $3d - t_{2g}$ band towards E_F together with a decrease of its band width (Fig. 3). Note that for the 11 nm case, the LDOS shows a weak resonance (virtual bound state) at E_F, whose spectral weight increases with decreasing size. Consequently, $N_{\rm Fe}(E_F)$ increases to values larger than the Stoner limit: $N_{\rm Fe}(E_F) = 2.5$, 1.8, and 1.3 states/eV-atom for $d_{\rm XRD} = 5$, 8, and 11 nm, respectively. The results, shown in Fig. 4, clearly corroborates our observation that Fe impurities in Nb nanoparticles with size ≤ 11 nm are magnetic. The onset of a local moment for Fe in nano-Nb below 11 nm is more clearly visible in the spin polarized $3d$ DOS of Fe (Fig. 3), which begins to show exchange splitting that increases with decreasing sizes. The magnitude of the Fe moment, shown in Fig. 4, increases from $0.46\mu_B$ at 11 nm to $2.14\mu_B$ at 5 nm (Table I), in reasonable agreement with the values of $\mu_{\rm Fe}$ estimated from $\beta(T)$. We point out that calculations using $2 \times 2 \times 2$ and $4 \times 4 \times 4$ supercells for the 5 nm sample yielded similar values of $\mu_{\rm Fe}$ (2.44 and $2.19\mu_B$, respectively), implying that these results are relatively independent of the supercell dimension and genuinely reflect the effect of size reduction. The results also corroborate our earlier conclusion that the Fe atoms occupy substitutional sites in Nb hosts. Note that interstitial Fe impurity in all nano-Nb hosts show zero moment. We have also calculated the magnetic hyperfine field of Fe, B_{hf} (Table I), which appears concomitantly with the onset of local moment and expectedly increases with decreasing size. Thus, our *ab initio* calculations reveal

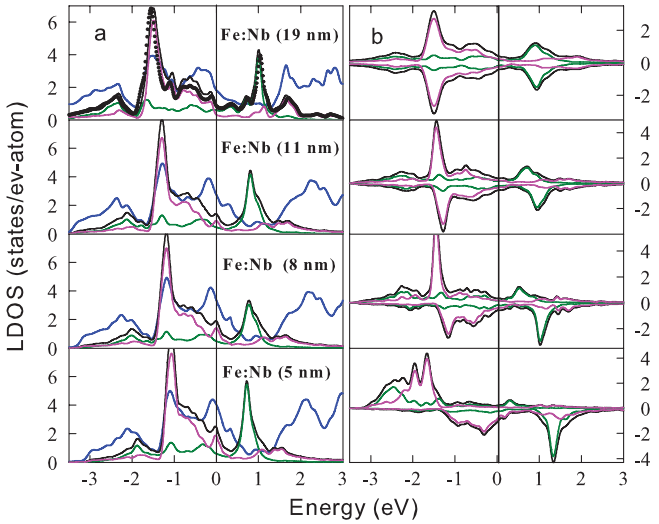

FIG. 3 (color). LDOS of Fe impurity in bulk and nano-Nb hosts: (a) unpolarized, and (b) spin polarized calculations. Color lines represent: black = Fe-d; green = t_{2g}; pink = e_g; blue = Nb-d ($\times 3$). Dotted line in top left panel corresponds to the LDOS of Fe in bulk Nb.

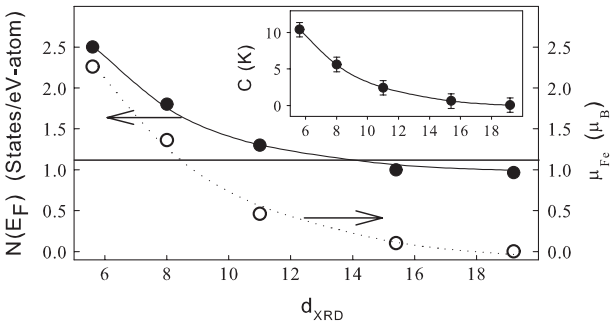

FIG. 4. Dependence of the calculated $N(E_F)$ (●) and magnetic moment (○) for Fe in nano-Nb host with mean lattice size $d_{\rm XRD}$. The size dependence of the Curie constant is shown in the inset. The solid lines are for visual guides.

a strong influence of the Nb lattice size on the magnetism of Fe, exhibiting a crossover from nonmagnetic to strong local moment behavior below a critical size of ≈ 11 nm. Note that such size reduction also causes a narrowing of the Nb-4d band, pushing it closer to the Fermi energy and resulting in a larger host density of states at E_F.

We now examine the effect of lattice size on the spin fluctuation of the Fe moments and argue that the host spin polarization has a strong influence on the Kondo temperature T_K. In general, the impurity moment interacts with the host-conduction electrons via a Kondo-type antiferromagnetic exchange, resulting in an effective loss (screening) of the moment below T_K which, depends on the interaction strength, $J\rho \approx |V_{kd}|^2\rho/\epsilon_d$. Here, V_{kd} is the hybridization strength, ϵ_d is the position of the Fe-3d states relative to E_F and ρ is the host DOS at E_F. A rough estimation, using the formalism of Ref. [18] yields $|V_{kd}| \approx 0.4$ eV for Fe in 5 nm Nb particles, consistent with the band width in Fig. 3. For larger Nb particles, V_{kd} increases due to smaller interatomic distance. Assuming ϵ_d to be ≈ 0.5 eV (centroid of Fe-3d band) and taking account of the size-induced increase in ρ, $J\rho$ come out as ≈ -0.36, which should lead to high $T_K \geq 5 \times 10^3$ K and hence nonmagnetic behavior of Fe in nano-Nb hosts. This contradicts our experimental observation of large μ_{Fe} and small T_K in nano-Nb smaller than 11 nm.

Why do the Fe moments in nano-Nb actually show a diminished Kondo interaction despite the strong hybridization? We suggest that a positive spin polarization of the host-conduction band electrons give rise to a ferromagnetic exchange interaction with the Fe moment and effectively lowers the Kondo temperature. To examine the host spin polarization produced by Fe in nano-Nb, we examine the induced moments on the Nb atoms surrounding the Fe impurity (Table I). The positive moments on the nearest neighbor (nn) Nb indicate ferromagnetic spin polarization of the Nb-4d electrons, while the negative moments at the second and third near neighbor sites are consistent with antiferromagnetic polarization of the host-conduction electrons. The magnitude of the ferromagnetic spin polarization increases with decreasing size of the host matrix. The resulting ferromagnetic interaction between Fe-d and the nn Nb moment can effectively decrease the Kondo coupling $J\rho$ and thus reduce T_K. The calculations presented above support our proposition that positive host spin polarization can diminish T_K substantially, as has been observed in many bulk alloys [3,19]. They are also consistent with our earlier results [8] in nano-Cu, though an enhanced antiferromagnetic $s-d$ interaction increases the T_K in nano-Ag, as expected. It is, however, important to note that—unlike most metals including Ag and Cu, in which the lattice constant shows little change with size—Nb exhibits a relatively large lattice expansion with decreasing size.

In conclusion, we have studied the local magnetism of isolated Fe impurities in nanocrystalline Nb hosts. Measurements of the local susceptibility and 3d spin relaxation rates, combined with *ab initio* electronic structure calculations, show a strong influence of lattice size on Fe magnetism, particularly on its spin fluctuation behavior. We have shown that a size-induced lattice expansion shifts the Fermi level and causes large enhancements in the local density of states, allowing the formation of local moments on Fe atoms in nanocrystalline Nb below a critical size of 11 nm, as opposed to its nonmagnetic nature in bulk Nb. Our results also illustrate that ferromagnetic spin polarization of host-conduction band electrons can reduce the Kondo coupling and stabilize the Fe moments. This work should provide an important basis for the general understanding of the magnetic behavior of isolated impurities in metallic hosts with reduced dimensions.

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