Size-induced crossover from itinerant to localized magnetism observed for isolated Fe impurities embedded in different structural polymorphs of silver

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Measurements of the local susceptibility and spin relaxation rate for isolated Fe atoms implanted in the nanocrystalline hexagonal phase of Ag (4*H*-Ag) show a large orbital moment, in stark contrast with the spin-dominated itinerant magnetism in conventional face centered cubic Ag. The orbital moment observed for Fe in hexagonal Ag ($\approx 1 \mu_B$) is the largest among *d*-block hosts, and resembles *f*-electron magnetism, suggesting Hund's rule type local moment with strong spin-orbit coupling. Calculations based on density functional theory suggest that the crossover from itinerant to local moment behavior results from localization of Fe-3*d* states due to size-induced changes in unit cell volume and symmetry.

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An isolated transition metal atom in its ground state possesses both spin and orbital magnetic moments in accordance with the Hund's rules. In solids, however, the atomic spin and orbital moments are strongly reduced due to hybridization and crystal field effects. Isolated transition metal impurities embedded in nonmagnetic hosts are ideal candidates for studying the interplay of atomic and solid state effects. In particular, the formation of localized magnetic moments in such systems has been a topic of intense experimental and theoretical research, following the pioneering work of Friedel and Anderson [1,2]. The *d* electrons in transition metals are usually treated as itinerant and the magnetic moment of d impurities in metallic hosts is described by an effective spin $S_{\rm eff}$ with the orbital contribution quenched by the large crystal field (CF) and/or hybridization. Improved experimental and theoretical techniques have allowed studies of the local moment under various conditions, revealing the occurrence of very large orbital moments on Fe, Co, or Ni impurities embedded in hosts with sp-band electrons such as alkali and alkaline earth metals [3-11]. In contrast, the type of magnetism observed for 3d impurities in transition metal hosts including noble metals is essentially spin dominated, conforming to the itinerant picture [12]. Such contrasting observations raise some important questions: Can a Hund's rule moment survive for d impurities in transition metal hosts? Is there a crossover from localized to itinerant magnetism? What causes the quenching of orbital moment in *d* impurities; crystal field or hybridization?

We address these questions through experimental measurements of local susceptibility and spin relaxation rate of isolated Fe impurities implanted in different structural polytypes of Ag using the time differential perturbed angular distribution (TDPAD) technique, supported by *ab initio* calculations based on density functional theory (DFT). Note that Fe in noble metal hosts like Cu, Ag, and Au normally exhibits a spin-dominated moment with negligible orbital contribution [8,13–16]. Elemental silver, commonly occurring in the face centered cubic (fcc) structure, has several crystallographic variants (polytypes) that differ only in the sequence in which hexagonally close-packed atomic layers are stacked along the

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 $\langle 111 \rangle$ direction. A four-period hexagonal polytype with lattice parameters a = 2.88 Å and c = 10.0 Å can be kinetically arrested in the nanocrystalline state under specific conditions when using high pressure sputtering [17] or pulsed electrochemical deposition [18,19]. As the atomic volume in 4*H*-Ag is about 6% larger than that in the common, three-period fcc (3*C*-Ag) form, one should expect a reduced hybridization strength for *d* impurities embedded in 4*H*-Ag. Thus, lightly Fe-doped 4*H*-Ag should provide an attractive testing ground for studying the roles of symmetry and hybridization on the nature of the magnetic moment on *d* impurities in metallic hosts.

In this paper we report the observation of an unusually large orbital magnetic moment on isolated Fe impurity atoms in nanocrystalline, hexagonal 4*H*-Ag, in contrast to the spin-dominated local moment in 3*C*-Ag that is ascribed to itinerant electrons. *Ab initio*, DFT-based electronic structure calculations suggest that the high orbital moment of Fe in 4*H*-Ag arises from enhanced localization of Fe-*d* electrons, originating from size-induced changes in unit cell volume and symmetry.

About 20 μ m thick films of 4*H*-Ag were electrodeposited on 100 μ m thick fcc silver foils (Alfa Aeser, 99.998%) by a conventional two-electrode process with a 1 cm diameter silver rod (99.95%) as anode. The aqueous electrolyte solution consisted of silver nitrate, citric acid, and boric acid. A periodic square wave potential consisting of 200 mV pulses of 5 s duration was applied at 10 s intervals for a total duration of 6 h. X-ray diffraction (XRD) and electron microscope data [20] confirmed that the as-prepared samples were densely packed, nanocrystalline, phase-pure, 4*H*-Ag films with a coherently diffracting domain size of 20(5) nm obtained from XRD line profile analysis. Details of synthesis and characterization are available in Ref. [19].

The local magnetic susceptibility of Fe in 3*C* (fcc) and 4*H* (hcp) Ag hosts was obtained from the measured hyperfine interaction of the 10⁺ isomeric state in ⁵⁴Fe ($T_{1/2} = 360$ ns, $g_N = 0.728$) produced by the heavy ion reaction ⁴⁵Sc(¹²C, p2n)⁵⁴Fe. The experiments were carried out at the Pelletron Accelerator Facility, TIFR using a 42 MeV pulsed ¹²C beam. The recoiling ⁵⁴Fe nuclei were implanted deep ($\approx 1 \mu m$) inside the host matrix at concentrations well below 1 ppm [21,22] ensuring negligible impurity-impurity interaction.



FIG. 1. Spin rotation spectra R(t) (left panel) and their Fourier transforms (right panel) for ⁵⁴Fe in 3*C* and 4*H*-Ag.

Spin rotation spectra of the γ rays from ⁵⁴Fe isomeric state were recorded in the temperature range 15–300 K and an applied magnetic field $B_{\text{ext}} = 20$ kG, using high purity Ge detectors placed at ±45° and ±135° with respect to the beam direction. For further experimental details, see Refs. [21–23].

Typical spin rotation spectra R(t) and their Fourier transforms for ⁵⁴Fe in 3C and 4H-Ag (Fig. 1) exhibit a single interaction frequency with high anisotropy, which indicated that the implanted Fe atoms were located at well defined-probably substitutional—lattice sites. The Larmor frequency ω_L and the nuclear relaxation time τ_N [21–23] were extracted by fitting the spectra to the function $R(t) = (3/4)A_{22}e^{-t/\tau_N}\sin[2(\omega_L t - \phi)].$ Here A_{22} is the anisotropy of the angular distribution pattern and ϕ is the phase factor arising from a finite bending of the incoming beam in the applied field. From the observed Larmor frequency $\omega_L = (g_N \mu_N B_{\text{eff}}/\hbar)$, we extract the effective magnetic field $B_{eff} = B_{ext} + B_{hf}$, where B_{ext} is the applied magnetic field and $B_{\rm hf}$ is the hyperfine field at the probe nuclear site. For paramagnetic ions: $B_{\text{eff}} = \beta B_{\text{ext}}$, where β is the paramagnetic enhancement factor and $\beta - 1 = B_{\rm hf}/B_{\rm ext}$ is a measure of the local susceptibility χ_{loc} of the impurity atom. In general, a negative $B_{\rm hf}$ is believed to arise from the spin magnetic moment of the impurity atom via Fermi-contact interaction, while a positive $B_{\rm hf}$ is ascribed to orbital magnetic moment. Hence, the corresponding local susceptibility $\chi_{\rm loc}({\rm spin}) < 0$, while $\chi_{\rm loc}({\rm orb}) > 0$, such that $\beta_{\rm spin}(T) < 1$ and $\beta_{\text{orb}}(T) > 1$. A measurement of $\beta(T)$ therefore identifies the nature of the magnetic moment on the impurity atom, with $\beta(T) = 1$ implying nonmagnetic behavior.

The strongly temperature dependent local susceptibility of Fe in bulk 3C-Ag, nano 3C-Ag, and nano 4H-Ag (Fig. 2) indicates that the magnetic moment on Fe is reasonably high. More significantly, there is a clear qualitative difference in the nature of the magnetic behavior of Fe in the hexagonal and cubic forms of Ag. While Fe atoms in 3C-Ag exhibit negative local susceptibility $[\beta(T) < 1]$, reflecting spin-dominated behavior, they show a large positive $\chi_{loc}(T)$ [$\beta(T) > 1$] in 4H-Ag, indicating an overriding contribution of the orbital moment. The observed $\beta(T)$ could be fitted to the Curie-Weiss law: $\beta(T) - 1 = C/(T + T_K)$, yielding C = -4.8(3), $T_K =$ 2.1(8) K for bulk 3C-Ag and C = 21.4(5) K, $T_K = 4(2)$ K for 4*H*-Ag. Here T_K is the Kondo temperature. A comparison of the susceptibility data for Fe in nano-4H-Ag, nano-3C-Ag (with similar grain sizes), and bulk-3C-Ag (Fig. 2) rules out the influence of grain size on the observed differences between the two Ag polytypes.



FIG. 2. Local susceptibility $\beta(T)$ of ⁵⁴Fe in bulk 3*C*-Ag (triangles) and nano-4*H*-Ag (circles). Data from nano (\approx 20 nm) 3*C*-Ag (from Ref. [24]) are also shown. The solid lines are fits to the Curie-Weiss law. Inset shows the relaxation time $\tau_N(T)$ in bulk 3*C*-Ag and nano-4*H*-Ag. The solid lines are fits to the Korringa relation (see text).

We first discuss the magnetism of Fe in 3*C*-Ag. The spin magnetic moment of Fe [indicated by $\beta(T) < 1$] was extracted from the Curie constant *C*, expressed as $C = g\mu_B(\tilde{S} + 1)B(0)/3k_B$, where \tilde{S} is the effective spin on the impurity atom and *B*(0) is the hyperfine field at T = 0. Taking B(0) = -40(5) kG [13,14,24], we obtain the local spin moment of Fe: $\mu_{\text{Fe}} = 3.3 \pm 0.4 \ \mu_B$ ($\tilde{S} \approx 1.5$). The magnitude of B(0) (-40 kG) is significantly smaller than the values observed in the isoelectronic hosts Cu (-150 kG) and Au (-200 kG) [14] and reflects a small orbital moment of $\approx 0.2 \ \mu_B$ in 3*C*-Ag, consistent with theoretical estimates from DFT [8,15].

Next, we discuss the case of Fe in 4*H*-Ag. If we take $\tilde{S} = 1.5$ (which is consistent with the spin moment obtained from our DFT calculations discussed below), we obtain B(0) =+190 kG. A positive hyperfine field can originate from selfpolarization of valence electrons and/or an unquenched orbital moment. Taking the core polarization field $B_{\rm hf}^{\rm cp} \approx -390 \, \rm kG$ (as obtained from the hyperfine coupling constant α_{CP} = $-120 \text{ kG}/\mu_B$ [15,25]), our data on 4H-Ag implies a net positive field of +580 kG. Such a huge positive B(0) is unlikely to arise from self-polarization of valence electrons of the impurity atom. We are therefore forced to conclude that the observed positive hyperfine field of Fe in 4H-Ag arises mainly from a large orbital magnetic moment μ_{orb} on the Fe atoms. Taking the orbital hyperfine coupling constant $\alpha_{\rm orb} \approx 600 \text{ kG}/\mu_B$ [10], we estimate $\mu_{\rm orb} \approx 1 \mu_B$ for Fe, corresponding to an effective orbital angular momentum $\tilde{L} \approx 1$. Note that even if we assume the valence electron contribution to B(0) to be as high as +160 kG, as observed for Fe in Au [15], the magnitude of orbital moment of Fe in 4*H*-Ag would still be higher than 0.7 μ_B . We further note that any uncertainties (within stated limits) in the hyperfine coupling constants do not significantly affect the above orbital moment. Clearly the size-induced structural change in Ag plays a crucial role on the magnetism of the embedded Fe atoms. To our knowledge, the orbital moment of Fe observed in 4*H*-Ag ($\approx 1 \mu_B$) is the largest seen for a 3*d* impurity in *any* transition metal host, irrespective of crystal structure [26–28].

The spin rotation spectra R(t) of ⁵⁴Fe (Fig. 1) show temperature-dependent damping, more clearly visible in 4H-Ag. Considering the narrow distribution width of ω_L and the strong magnetic response [Fig. 2(a)], it is reasonable to assume that the spectral damping arises from dynamic fluctuation of the Fe magnetic moment. An estimate of the spin fluctuation rate $\tau_{\rm SF}^{-1}$ was obtained from the measured relaxation time τ_N using the relation $\tau_{\rm SF}^{-1} = 2[g_N \mu_N B(0)/\hbar]^2 (\tilde{S}+1) \tilde{S}^{-1} \tau_N$ [24]. The spin relaxation time τ_N for Fe in 3*C*-Ag is virtually temperature independent (see inset, Fig. 2). On the other hand, τ_N varies strongly with temperature and exhibits Korringalike behavior $(\tau_N \propto \tau_{\rm SF}^{-1} \propto T)$ in the case of Fe in 4*H*-Ag. The τ_N observed at 25 K yields $\tau_{SF}^{-1} \approx 4 \times 10^{11}$ s⁻¹, which corresponds to a spin linewidth of ≈ 2 meV, a value comparable with that reported for Fe in alkali metals [3]. The τ_N data, analyzed within Kondo model [24,29], yield $T_K = 1.5$ and 2.9 K for Fe in 3C-Ag and 4H-Ag, respectively, agreeing reasonably well with the values obtained from the $\chi_{loc}(T)$ data discussed earlier. The low values of T_K observed from our $\beta(T)$ and $\tau_N(T)$ data reflect the high stability of the Fe moment in bulk 3C-Ag as well as nano-4H-Ag.

Further insight into the problem was obtained from *ab initio* electronic structure calculations for an isolated Fe impurity in 3C- and 4H-Ag performed within the local density approximation (LDA) of DFT using the all-electron augmented plane wave + local orbital (APW + lo) technique as implemented in the WIEN2k package [30]. Calculations were carried out with and without spin polarization using a 108-atom supercell (107 Ag + 1 Fe) constructed with $3 \times 3 \times 3$ units of 3C-Ag with the experimental lattice constant. For 4H-Ag we used a $3 \times 3 \times 2$ supercell with 72 atoms. To resolve the spin and orbital components of the Fe impurity moment we applied the LDA+U scheme, taking account of the spin-orbit interaction using the Coulomb parameter U = 2.5 eV and the exchange interaction strength J = 0.9 eV [32–34]. Further details on the calculations can be found in Ref. [31].

We first discuss the results from the nonmagnetic calculations and examine the size and structure dependent changes in the local density of states (LDOS) of Fe. Figure 3 shows that the Fe-d states are sharply peaked near the Fermi energy E_F , implying the formation of a virtual bound state (VBS), with the Fe LDOS $N_l(E_F) \ge 5$ states/eV atom. Taking the exchange parameter I = 0.925 eV [21,35], we find that the Stoner criterion for moment formation $IN_l(E_F) > 1$ is satisfied for both 3- and 4H-Ag. The LDOS results also imply that the crystal field splitting (energy separation between the e_g and t_{2g} bands) is quite small (≤ 0.2 eV) for Fe in both phases of Ag. Note that the VBS in nano-4H-Ag become narrower and shifts closer to E_F than in bulk 3C-Ag. Consequently, the hybridization between the d band electrons of Fe and Ag gets reduced in 4H-Ag, and we shall later argue that this is the major factor that leads to the large orbital magnetism of Fe in 4H-Ag. The existence of a large magnetic moment on Fe is more clearly visible in the spin-polarized LDOS results (Fig. 3, left panel) which shows a large splitting $(\approx 2.5 \text{ eV})$ between the majority and minority spin bands. The spin and orbital magnetic moments computed from LDA+U calculations together with the hyperfine fields are displayed in Table I.



FIG. 3. LDOS of Fe in bulk 3*C*-Ag host (a) and (b) and nano-4*H*-Ag host (c) and (d). Calculations for both from unpolarized (a) and (c) and spin polarized (b) and (d) LDOS are shown. Line colors: black is Fe-*d*; red and green in (a) show Fe- d_{e_g} and Fe- $d_{t_{2g}}$, respectively; cyan, dark red, and pink in (c) denote $d - z^2$, $d - (x^2y^2 + xy)$, and d - (xz + yz) of Fe. Dashed blue in (b) and (d) denote Ag-4*d*. The vertical dashed lines mark the position of E_F .

We observe that the spin magnetic moments and the corresponding core polarization hyperfine fields of Fe in bulk 3C- and nanocrystalline 4H-Ag have similar magnitudes. For Fe in 3C-Ag we obtain an orbital magnetic moment of 0.23 μ_B in agreement with theoretical calculations [8,15]. Furthermore, the net hyperfine field $B_{\rm hf}^{\rm tot} = B_{\rm hf}^{\rm cp} + B_{\rm hf}^{\rm val} + B_{\rm ofb}^{\rm orb}$ comes out as -30 kG, in good agreement with our experimental results. Furthermore, our calculations in 4H-Ag show an orbital magnetic moment of 0.85 μ_B for Fe with $B_{\rm hf}^{\rm tot} = +230$ kG, again corroborating our experimental observations.

To examine the role of the crystal symmetry of the Ag host on the orbital magnetism of Fe, we performed additional calculations for 3*C*-Ag, setting the unit cell volume *equal* to that for 4*H*-Ag. The calculated spin and orbital moments of Fe for this case are $\mu^{\text{spin}} = 3.04 \,\mu_B$ and $\mu^{\text{orb}} = 0.48 \,\mu_B$. The corresponding hyperfine fields are $B_{\text{hf}}^{\text{spin}} = B_{\text{hf}}^{\text{val}} + B_{\text{hf}}^{\text{val}} = -150 \text{ kG}$ and $B_{\text{hf}}^{\text{orb}} = +259 \text{ kG}$, respectively, yielding $B_{\text{hf}}^{\text{tot}} = +109 \text{ kG}$. This shows that though a pure expansion of the unit cell in 3*C*-Ag does increase the orbital moment to some extent, the main reason for the observed enhancement in 4*H*-Ag appears to stem from symmetry change from cubic to hexagonal. We point out that a reduction in the local susceptibility of Fe has been earlier observed in nanocrystalline 3*C*-Ag, and was ascribed to an increase in the Kondo temperature. The above discussions suggest that the reduction in $\beta(T)$ observed earlier in nanocrys-

TABLE I. Calculated magnetic moments (in μ_B) and hyperfine fields (in kG) for Fe in 3*C*- and 4*H*-Ag. B_{hf}^{tot} is the total hyperfine field with B_{hf}^{cp} , B_{hf}^{val} , B_{hf}^{orb} , and B_{hf}^{tot} being contributions from core polarization, valence electrons, and orbital moment.

Host	$\mu_{ m spin}$	$\mu_{ m orb}$	$B_{ m hf}^{ m cp}$	$B_{ m hf}^{ m val}$	$B_{ m hf}^{ m orb}$	$B_{ m hf}^{ m tot}$
3 <i>C</i> -Ag	3.06	0.23	-368	212	126	$-30 \\ 230$
4 <i>H</i> -Ag	3.11	0.85	-376	154	452	

talline 3*C*-Ag may have *partly* arisen from a slight increase in the orbital moment due to an expansion of the unit cell.

How do we understand the greatly enhanced orbital moment on Fe in 4H-Ag vis-a-vis bulk 3C-Ag? We have seen that our experimental data on $\chi_{loc}(T)$ for Fe in 4*H*-Ag cannot be reconciled with the itinerant spin magnetic moment scenario. In fact, the observation of a large orbital moment, a relatively high positive B(0) and a narrow 3d spin linewidth, all indicate strong intra-atomic correlations, and suggest that the magnetic moment of Fe in 4*H*-Ag be described by $\mu_{\text{Fe}} = g_{\tilde{J}} \mu_B \tilde{J}$, in terms of an *effective* total angular momentum: $\tilde{J} = \tilde{L} + \tilde{S}$, obtained from Hund's second rule with LS coupling, but with \tilde{J} being reduced from its "atomic" value by crystal field and/or hybridization effects. DFT calculations, however, indicate weak crystal field splittings ($\approx 0.2 \text{ eV}$) in both cases. We ascribe our observations mainly to the significant reduction in the Fe-3d width in the LDOS (especially for the VBS in the spin-down band) between 3C-Ag and 4H-Ag, as seen in Fig. 3. A reduction in the VBS width suggests stronger localization of Fe-d electrons in 4H-Ag due to diminished hybridization [2] resulting from the size-induced expansion in the unit cell volume. A close examination of the results from the LSDA+U

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calculations shows that the Fe-3*d* spin-up band is nearly full in both 3*C*-Ag and 4*H*-Ag: the orbital moment originates mainly from Fe-*d* spin-down electrons. In 3*C*-Ag, the Fe-3*d* spin-down *m* substates have similar population giving rise to a small orbital moment of $\approx 0.23 \ \mu_B$. On the other hand, the highly localized Fe-3*d* spin-down states in 4*H*-Ag mostly occupy $m_l = 0$ and $m_l = 2$ states, leading to a higher orbital moment of $\approx 1 \ \mu_B$.

In conclusion, local susceptibility measurements using TDPAD clearly reveal an unusually large orbital moment for isolated Fe atoms in the size-stabilized hexagonal polymorph of Ag. This reflects Hund's rule magnetism, as opposed to the usual, spin-dominated itinerant behavior in conventional face-centered cubic Ag. The experimental observations are corroborated by *ab initio*, DFT-based electronic structure calculations, which suggests that the crossover from itinerant to Hund's rule type local moment arises mainly from enhanced localization of Fe-*d* electrons, originating from size-induced changes in unit cell volume and lattice symmetry, overriding the contribution from crystal field effects.

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