

Local Magnetism of Isolated Mo Atoms at Substitutional and Interstitial Sites in Yb Metal: Experiment and Theory

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We have observed large $4d$ moments on isolated Mo atoms at substitutional and octahedral interstitial lattice sites in Yb metal, showing Curie-Weiss local susceptibility and a Korringa-like spin relaxation rate. The interstitial Mo atoms, despite strong hybridization with the Yb neighbors, show rather small Kondo temperature ($T_K \leq 60$ K), implying high moment stability. While magnetism of Mo at the substitutional site is consistent with Kondo-type d - sp interaction, we suggest that moment stability at the interstitial site is strongly influenced by ferromagnetic polarization of Yb- $4f5d$ band electrons.

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The formation and stability of local magnetic moments on d impurities in metallic hosts has been a topic of intense experimental and theoretical investigations over the past several years. While extensive studies have been made for several $3d$ impurities [1,2], much less information is available on the magnetism of $4d$ atoms in metals. In general, the d electrons in $4d$ metals are regarded as being itinerant and do not show tendency towards local moment formation. Recently, applying time differential perturbed angular distribution/correlation (TDPAD/TDPAC) methods, strong magnetic behavior has been observed for some substitutional $4d$ impurities in few metals and alloys [2,3]. The results revealed that, similar to the behavior observed for $3d$ impurities, magnetism of $4d$ ions in metals strongly depends on the type of conduction electrons in the host. Furthermore, it has been argued that moment stability measured by the Kondo temperature T_K is strongly influenced by induced spin polarization of host band electrons.

In view of these aspects of magnetism for substitutional $3d$ and $4d$ impurities in metals, one can ask: can a local moment occur on $3d/4d$ atoms at interstitial lattice sites also? If so, how stable are the moments? What is the magnitude and sign of host spin polarization and how do they influence the impurity magnetism? Intuitively, due to reduced interatomic distances and the consequent increase in the hybridization strength, one would expect suppressed magnetism for d atoms at interstitial lattice sites. However, a large $3d$ moment has recently been observed for Fe at interstitial sites in fcc Yb metal [4]. Hitherto, magnetism of $4d$ atoms at interstitial lattice sites in a metal has not been investigated. In this Letter we report experimental and theoretical studies on the magnetism of isolated Mo impurity atoms at substitutional and interstitial lattice sites in Yb metal. The results, obtained from TDPAD measurements and local spin density (LSD) calculations, show that Mo atoms occupying substitutional and octahedral interstitial sites possess large stable $4d$ moments with rather small

T_K values. We show that lattice site dependent magnetism of Mo, especially the moment stability, is strongly influenced by the sign and strength of host conduction electron spin polarization.

TDPAD experiments were carried out at the TIFR/ BARC Pelletron accelerator facility, Mumbai. We used the 8^+ isomer in ^{94}Mo ($T_{1/2} = 98$ ns, $g_N = 1.31$) as a nuclear probe for the detection of the magnetic response. Heavy ion reaction $^{82}\text{Se}(^{16}\text{O}, 4n)^{94}\text{Mo}$ with a pulsed ^{16}O beam of energy 62 MeV was used to produce and recoil implant the probes in Yb hosts. The estimated concentration of Mo in Yb was less than 1 ppm. Spin rotation spectra $R(t)$ were recorded in the temperature range 10 to 300 K by applying a magnetic field of 2 T. Further details on the experimental method can be found in Ref. [5]. Measurements were performed in fcc and hcp Yb. Following Ref. [6], fcc Yb could be obtained by rolling a piece of pure (9.99%) metal to a thickness of about 5 to 10 mg/cm². To get the hcp phase, a thin disk of Yb metal was annealed at 400 °C for 12 hours followed by repeated cycles of dipping in liquid nitrogen and warming to 300 K. The crystal structures of the samples were verified by x-ray diffraction measurements.

Figure 1 shows some examples of spin rotation spectra, $R(t)$ for ^{94}Mo in fcc and hcp Yb along with their Fourier transforms. The spectra show superposition of three frequency components arising from Mo atoms at different lattice sites. They were fitted by the function [5]: $R(t) = \sum_i A_i \exp(-t/\tau_{Ni}) \sin[2(\omega_L t - \theta)]$ to extract the amplitude A , Larmor frequency ω_L , and the nuclear spin relaxation time τ_N of each component. Figure 2 shows the local susceptibilities, $\chi_{\text{loc}}(T) = \beta(T) - 1$ of Mo deduced from the relation $\omega_L(T) = \hbar^{-1} g_N \mu_N B_{\text{ext}} \times \beta(T)$. It can be seen that β for two of the components in fcc as well as hcp Yb strongly varies with temperature which could be fitted to a Curie-Weiss law: $\beta(T) - 1 = C/(T + T_K)$. The Curie constants C for the two components, in both

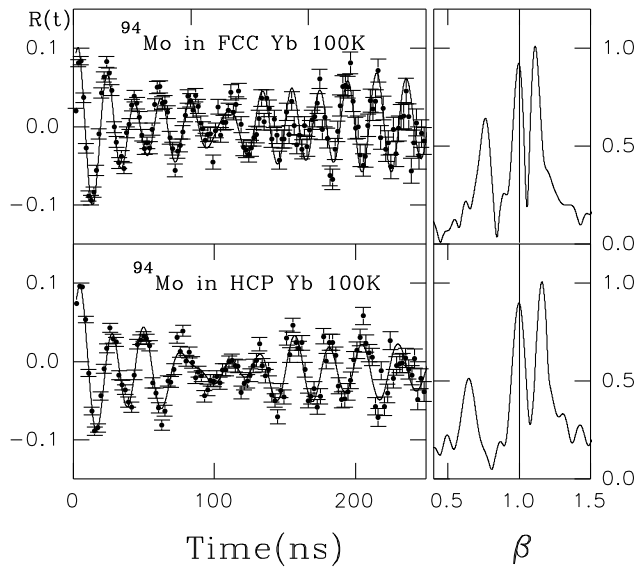


FIG. 1. Spin rotation spectra, $R(t)$ (left panel) and their Fourier transforms (right panel) for ^{94}Mo in fcc and hcp Yb.

phases of Yb, were found to be $+15(2)$ and $-32(2)$ K. Furthermore, the corresponding nuclear relaxation times τ_N , shown in Fig. 3, exhibit Korringa-like behavior ($\tau_N \propto T$). Both these features reflect strong local magnetism of Mo. From the amplitudes (A_i), it turns out that nearly 50% of the implanted Mo atoms in fcc as well as hcp Yb show a positive Curie constant while a fraction of $\sim 25\%$ exhibit negative C value. The remaining $\sim 25\%$ show temperature independent χ_{loc} with $\beta(T) = 1.00 \pm 0.02$. Tentatively, we assign the components characterized by $\beta(T) < 1$ and

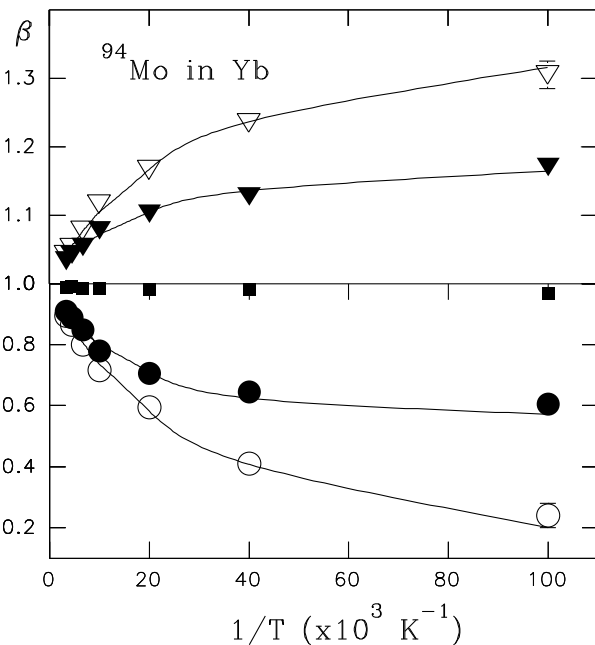


FIG. 2. Local susceptibility $\beta(T)$ of Mo in fcc (filled symbols) and hcp (open symbols); Yb as a function of $1/T$. The solid lines correspond to fits by the Curie-Weiss law: $\beta(T) - 1 = C/(T + T_K)$.

$\beta(T) > 1$, respectively, to substitutional and octahedral interstitial sites. The third fraction [$\beta(T) = 1$] presumably corresponds to a tetrahedral interstitial site. Since fcc and hcp Yb have identical near neighbor environments, for our later discussion of Mo magnetism, we mainly consider the components ascribed to substitutional and octahedral interstitial sites in fcc Yb.

To get theoretical understanding on the lattice site dependent magnetism of Mo in the Yb host, we have performed first-principles spin polarized, semirelativistic supercell electronic structure calculations within the local spin density approximation (LSDA), employing the tight binding linear muffin-tin orbital method in atomic sphere approximation (TB-LMTO-ASA) [7] and von Barth-Hedin [8] parametrization for the exchange correlation potential. Calculations were carried out for a single Mo impurity at substitutional as well as octahedral interstitial sites, using cubic supercells (space group $Pm\bar{3}m$) of a dimension twice the lattice constant of fcc Yb, with 32 (33 for interstitial case) atoms and treating Yb-4*f* as band electrons. In order to accommodate the large Mo impurity in the interstitial site without violating the overlap criterion prescribed by ASA, the nearest neighbor (nn) Yb atoms had to be relaxed outwards by at least 5% of the nn distance. The next nearest neighbor atoms were left unrelaxed thus keeping the unit cell volume intact. No relaxation was necessary for treating the substitutional case.

Figure 4 shows the up and down spin local density of states (LDOS) of Mo-*d* electrons. The results showing large splitting of the two spin subbands clearly indicate the presence of high local 4*d* moments on Mo. The calculated moments, summarized in Table I, turn out to be $3.56\mu_B$ for substitutional and $1.12\mu_B$ for the interstitial Mo atoms. For further confirmation of the rather high moment of Mo, especially at the interstitial site, we performed additional calculations using a spin polarized full-potential

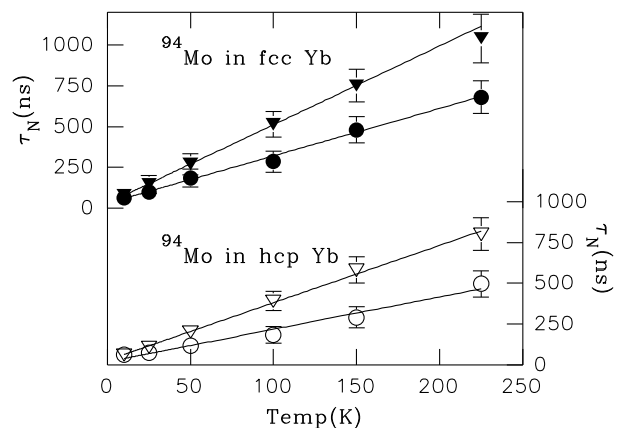


FIG. 3. Nuclear relaxation time τ_N as a function of temperature for ^{94}Mo in fcc Yb (filled symbols) and hcp Yb (open symbols). The linear dependence of τ_N with T (solid lines) is indicative of the Korringa-like relaxation process (see text).

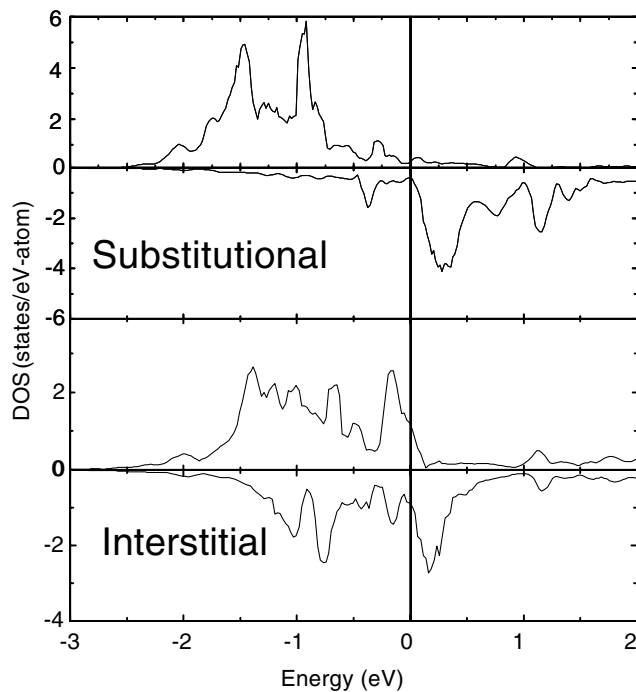


FIG. 4. Local density of states (LDOS) for a Mo impurity in fcc Yb host occupying substitutional and relaxed (5%) octahedral interstitial sites.

linearized augmented plane wave (FLAPW) method as implemented in the WIEN code [9]. The resulting Mo moments $3.21\mu_B$ for substitutional and $1.29\mu_B$ for the interstitial sites closely agree with the LMTO-ASA results. For the interstitial case, calculations with higher lattice relaxation, 17% taken from assumption of hard sphere atomic radii, yielded a larger moment $\sim 1.8\mu_B$ ($2.1\mu_B$ from the FLAPW method).

Coming back to the experimental results, the Mo magnetic moments can be estimated from the Curie constants using $C = g(S + 1)\mu_B B(0)/3k_B$ [5] where $B(0)$ is the hyperfine field at 0 K. For a half filled $4d$ shell, neglecting orbital contribution, the measured $B(0)$ consists of a negative core polarization field, B_{CP} and a positive term (B_{val}) arising from the valence electrons. The net spin contact hyperfine fields for many $4d$ impurities have been found to lie between -200 and -280 kG [10]. Assuming

TABLE I. Summary of Kondo temperature T_K , hybridization strength V_{kd} , and calculated (LMTO method) magnetic moments m_0 for a Mo impurity at substitutional and relaxed (5% and 17%) octahedral interstitial lattice sites in fcc Yb. m_1 and m_2 are the induced moments at nearest and next nearest Yb atoms.

	Substitutional	Interstitial
T_K (K)	60	60
V_{kd} (eV)	0.104	0.256
m_0 (μ_B)	3.56	1.12(1.77 ^a)
m_1 (μ_B)	-0.013	0.12(0.29 ^a)
m_2 (μ_B)	0.008	0.0(0.06 ^a)

^aCorresponds to results obtained with 17% lattice relaxation.

$B(0) = -240$ kG, the Mo moment for the minority fraction [$\beta(T) < 1$] turned out to be $3.96\mu_B$ which is close to the value calculated for the substitutional site. This supports our earlier attribution of the $\beta(T) < 1$ component to Mo atoms at the substitutional lattice site. For the majority fraction, the observed $\beta(T) > 1$ behavior implies $B(0)$ to be positive which can arise from a larger contribution from the valence $5s$ electrons and a much reduced value of B_{CP} . The exact value of $B(0)$, though difficult to calculate, a reasonable estimate of it from the τ_N data [11] which came out to be $\sim +19 \pm (2)$ T. With this $B(0)$, the Mo moment for the majority fraction was found to be $1.5 \pm 0.3\mu_B$, in accordance with the values calculated for the octahedral interstitial site. This gives credence to our assumption that the component with $\beta(T) > 1$ arises from Mo atoms at the octahedral interstitial site. The above site assignment is also supported from results reported for Fe in Yb [4]. Here, we like to emphasize that any uncertainty in $B(0)$ and the consequent spread in the Mo moments does not influence the main conclusions of this work.

Next we examine spin fluctuation of Mo magnetic moments in Yb which can be scaled with the Kondo temperature, T_K . The latter can be derived from the Curie-Weiss fit of $\beta(T)$ data. The measured $\beta(T)$ corresponding to substitutional as well as interstitial sites in fcc Yb yielded $T_K = 60 \pm 10$ K. For Mo in hcp Yb the T_K values for the two sites were found to be 35 ± 5 K. An estimation of T_K could also be obtained from the spin relaxation rates τ_J extracted from the τ_N data [11,12]. The T_K derived from τ_N data again turn out to be similar for both substitutional and interstitial sites, being ~ 55 K for fcc Yb and ~ 20 K for hcp Yb. The low value of T_K , derived from both $\beta(T)$ and τ_N data, indicates rather small spin fluctuation implying high moment stability for Mo at substitutional as well as interstitial lattice sites.

Finally, by analyzing the Kondo temperatures of site specific Mo moments in Yb we show that magnetism, particularly moment stability, is strongly influenced by the sign and strength of spin polarization of host conduction band electrons. Starting from the Kondo model, instability of a magnetic moment is caused by antiferromagnetic exchange interaction between impurity- d and host conduction electrons. The degree of instability proportional to T_K is governed mainly by the Kondo resonance width [12] $\Gamma = \pi N(E_F)V_{kd}^2$, where V_{kd} is the hybridization strength. For Mo in divalent Yb host with dominantly sp -type conduction electrons, the hybridization strength can be roughly estimated using the procedure given in Ref. [13] and listed in Table I. Using these V_{kd} values the $T_K (= \Gamma/k_B)$ of substitutional Mo impurity in fcc Yb was found to be ~ 75 K in close agreement with the value 60 K measured experimentally. Furthermore, the magnetism of the substitutional Mo atom in Yb is consistent with the trend observed in alkali and alkaline earth metals [11,14] whereby the reduction in moment correlates with the hybridization strength. The above analysis shows that

magnetism of substitutional Mo in Yb can be well understood within the Kondo model. Extrapolating the same physical picture to a Mo impurity at the interstitial site, due to stronger hybridization strength (see Table I), one would expect the moment to be highly unstable with $T_K > 400$ K leading to nonmagnetic behavior with $\beta(T) = 1$. Instead, interstitial Mo atoms in Yb show a rather stable moment with Curie-Weiss type $\beta(T)$ and a low $T_K \leq 60$ K.

What is the physical reason for the high moment stability of the interstitial Mo atom in Yb? To understand this, we look into the host spin polarization by examining the induced moments at the Yb site. The results listed in Table I clearly reveal that sign and strength of host polarization for the interstitial site qualitatively differ from the features seen for the substitutional case. For substitutional Mo, the small negative moment at the Yb site, mainly arising from sp -band electrons, implies an antiferromagnetic polarization of host band electrons. In contrast, Yb atoms surrounding the interstitial Mo impurity show a substantial positive moment largely due to ferromagnetic polarization of $4f5d$ band electrons of Yb. From the results presented above, we believe that this induced ferromagnetic polarization causing strong interatomic interaction between Mo- $4d$ and host conduction electrons is mainly responsible for the high moment stability of interstitial Mo atoms in Yb. The features of host polarization found for interstitial Mo in Yb and its influence on T_K show striking similarity with the results observed for $3d$ and $4d$ impurities in some d band metals, viz., Pd and PdFe alloys [3,15,16]. As a plausible mechanism, we suggest that interatomic ferromagnetic interaction between Mo- $4d$ and host conduction band electrons can compete and successfully suppress T_K arising from antiferromagnetic d - sp exchange interaction and thereby stabilize the magnetic moment of Mo at the interstitial lattice site. The above physical picture is consistent with the prediction of recent theoretical calculations where a ferromagnetic interaction between the impurity and host conduction electrons has been shown to suppress the Kondo resonance at Fermi energy [17].

To conclude, combining TDPAD experiments with local spin density calculations, large $4d$ local moments have been observed for Mo atoms at substitutional and octahedral interstitial lattice sites of fcc and hcp Yb metal. While the magnetism of Mo for the substitutional site is consistent with the Kondo-type antiferromagnetic d - sp exchange interaction, we find that magnetism and Kondo temperature of an interstitial Mo atom are strongly influenced by fer-

romagnetic polarization of host Yb- $4f5d$ band electrons. The results and interpretations presented in this Letter provide an important basis for understanding local magnetism of interstitial d -impurities in a metallic host. They also yield insight on the key role of ferro- and antiferromagnetic host polarizations on the Kondo effect of magnetic atoms in general.

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