Observation of Magnetism of Fe at an Interstitial Site in a Metal Host

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Using perturbed angular (γ-ray) distribution techniques and in-beam Mössbauer spectroscopy, we have investigated the interstitial and substitutional site occupation and the site-specific magnetic behavior of implanted Fe impurities in fcc Yb. As a new feature, strong magnetism is observed for interstitial Fe atoms, which exhibit a rather stable local moment and Korringa-like spin dynamics. The essential experimental results are found to be consistent with the predictions of local spin density calculations, carried out for relaxed octahedral interstitial and for substitutional Fe sites in Yb. These combined results yield insight into basic features of magnetic moment formation and local structure at an interstitial site. [S0031-9007(97)02439-3]

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In contrast to the large number of studies of substitutional magnetic impurities, no reliable experimental information is available for the existence of a local magnetic moment at an interstitial lattice site in metallic hosts. Challenging motivations for studying magnetism and electronic structure at interstitial sites are provided by the expected drastic changes in basic parameters, e.g., in lattice volume and electron density. Any attempt at such a study has to overcome the difficulties in the production of interstitials; in addition, one requires a method with high local sensitivity to the magnetic response of the interstitials produced. The production of interstitial atoms in metals works reasonably well for self-interstitials and for light impurities (muons, H, B, C, N, and O), and much effort has been spent on investigating such systems, in particular, with respect to site location, formation energies, and diffusion processes. Also, $3d$ ions can be produced as self-interstitials in metals, e.g., by electron beam irradiation. However, for these cases no method seems to be available to disentangle the possible magnetic response of the very few interstitials from the many magnetic substitutional $3d$ ions. Moreover, one might speculate that the formation of a magnetic moment at interstitial sites seems rather unlikely. Naively, one would expect much more broad $3d$ band states and supressed atomic spin correlations at interstitial lattice sites as compared to substitutional sites, because the considerably reduced interatomic distances should lead to a much stronger $3d$-shell hybridization. As will be discussed below, however, such arguments should be regarded with caution.

In the central part of this work, we will present evidence that a $3d$ ion can be magnetic at an interstitial lattice site in a metal. After a series of test experiments, we have found Fe ions in an fcc Yb host to be a suitable system in which interstitial Fe exhibits readily measurable magnetic properties. In order to gain optimal information about the complex physics of site occupation and local magnetic and electronic properties at different lattice sites, we have applied two experimental and one theoretical method. Fe at interstitial as well as substitutional sites in fcc Yb has been produced and investigated by recoil implantation techniques combined with time differential perturbed angular distribution (TDPAD) and in-beam Mössbauer spectroscopy (IBMS) techniques. These methods provide the microscopic sensitivity necessary to observe the site-specific local properties. Magnetic behavior and isomer shift are found to be drastically different for the two Fe sites. The experiments are paralleled by local spin density (LSD) calculations, which give insight into the problem from the theoretical aspect as well.

The experiments were carried out at the ISL accelerator of the Hahn-Meitner-Institut in Berlin. For the TDPAD investigations, the 10^+, 360 ns isomeric state of ^{54}Fe was used as nuclear probe, produced and recoil implanted into Yb via the heavy ion reaction ^{45}Sc (^{12}C, $p2n$) ^{54}Fe by bombarding a thin ^{45}Sc foil with a pulsed ^{12}C beam at 42 MeV energy. For the IBMS experiments, an ^{40}Ar beam at 100 MeV passing through an ^{57}Fe foil was used to produce Coulomb excited ^{57}Fe probe atoms (with 100 ns half-life) which recoiled into Yb foils. For a more detailed description of the TDPAD method and some selected results we refer to Refs. [1,2]; basic features of methodical and physical aspects of the IBMS method have been reviewed in Ref. [3]. Here we simply point out that in both methods, the recoiling Fe nuclei are implanted deeply ($0.3-3$ μm) into the Yb host at a concentration well below 1 ppm, while the measurements which immediately follow implantation are performed on

an extremely short time scale (10 ns to 2 μs). Thus both methods yield almost identical sample preparation and ensure a comparable microscopic study of truly isolated Fe impurities even in the nonalloying system under study (compare Refs. [1–3]).

The Yb host material was prepared in a purified Ar atmosphere by rolling metal pieces to thicknesses between 0.1 and 1 mm. With this procedure, we avoided the formation of hcp Yb and produced material in the pure fcc phase [4], which was shown to be stable over the whole temperature range (10 to 300 K) of our measurements by means of x-ray analysis.

The spin rotation spectra for ^{54}Fe in fcc Yb exhibit clearly visible beat patterns arising from the presence of two components with quite different behavior of the Larmor frequencies ω_L and damping times τ_N (see the examples in Fig. 1). The two components correspond to Fe on distinct sites in the Yb lattice. The local susceptibilities $\beta - 1$, extracted from the relation [1] $\omega_L = \hbar^{-1}\mu_N g_N B_{ext}\beta$, are shown in Fig. 2. They indicate clear magnetic responses for both Fe lattice sites. From the observed amplitudes, it follows that the majority component, i.e., 60% of the Fe implants, possesses a negative slope in the local susceptibility vs temperature curve, whereas the minority component (about 15%) exhibits a positive slope. A fraction of about 25% does not contribute to the spin rotation pattern.

Complementary information is obtained for ^{57}Fe in fcc Yb from the Mössbauer spectra shown in Fig. 3. These spectra show a dominant single line with 60% of the spectral intensity, exhibiting a narrow width with no detectable quadrupole splitting and an isomer shift of $\delta = -0.26(2)$ mm/s (same calibration convention as used in Ref. [3]). Quite systematically, Fe on interstitial sites possesses a significantly more negative isomer shift than Fe on substitutional lattice sites, mainly because the much smaller interstitial volume leads to a more compressed valence s wave function and thus to an increased s electron density at the Fe nucleus. This has been consistently demonstrated by recent experiments and calculations for various Fe systems [3,5]. Therefore, by comparison of the relative intensities, we can consistently identify the 60% Mössbauer component with the 60% TDPAD component as being due to interstitial Fe atoms. The remaining 40% of the Fe implants yield a broadened spectral feature with positive isomer shifts in the range 0.2 to 0.6 mm/s (in the emission spectra of Fig. 3, to the left of the dominant single line). Comparing again the IBMS and the TDPAD data, we see that this feature must contain the fraction seen by TDPAD as the 15% minority site signal, as well as a fraction with locally perturbed Fe surroundings often found in IBMS experiments [3]. Because of its perturbed surroundings, the latter fraction is not detected in the phase-sensitive TDPAD experiment. We identify the 15% TDPAD signal as arising from (locally undisturbed) substitutional Fe atoms. In addition, these lattice site characterizations are strongly supported by our results for the magnetism of substitutional Fe and by the predictions of our LSD calculations for the isomer shifts (see below).

We have also investigated the possibility that internal lattice pressure in the Yb host surrounding the interstitial Fe site might cause a local valence transition in Yb from $4f^{14}$ towards magnetic $4f^{13}$ Yb ions, which in turn could induce magnetic hyperfine fields on the otherwise nonmagnetic Fe impurity. In order to test this possibility,

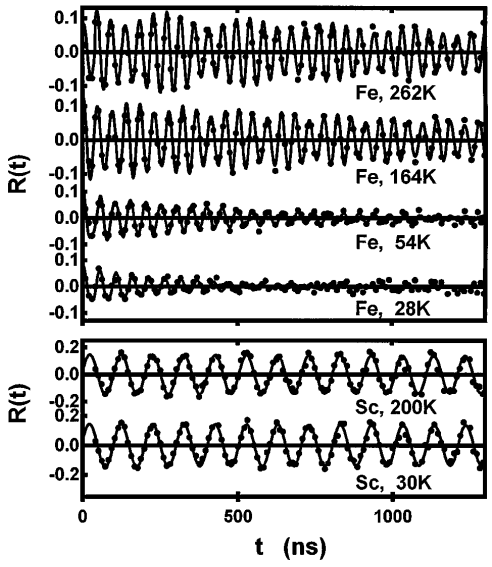

FIG. 1. Spin rotation spectra $R(t)$ for ^{54}Fe and ^{43}Sc ions implanted into Yb. The beat patterns in the Fe spectra are due to the superposition of different magnetic responses from the two Fe sites, the response from the interstitial site being dominant.

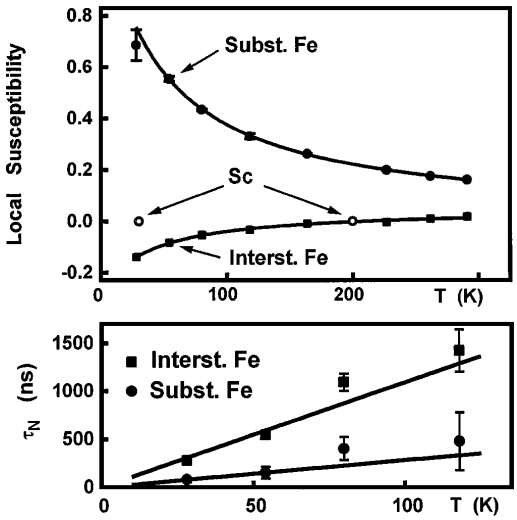

FIG. 2. Local susceptibilities fitted by a Curie-Weiss law (upper part), and nuclear relaxation times fitted by a Korringa law (lower part), for interstitial (squares) and substitutional (circles) Fe sites.

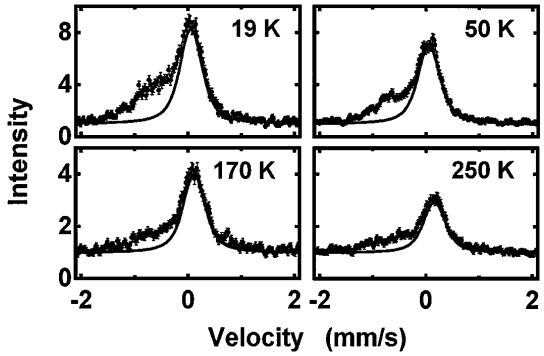

FIG. 3. Mössbauer emission spectra for ^{57}Fe in Yb measured vs a stainless steel absorber at room temperature. The dominant single line on the left corresponds to interstitial Fe.

we have studied the magnetic behavior of ^{43}Sc probe atoms [6] recoil implanted into Yb, with the result that no transferred hyperfine fields were detected on the even larger Sc impurity, which we reasonably expect to occupy both interstitial and substitutional sites [6,7]. With high sensitivity, all Sc implants are found to be clearly nonmagnetic in Yb (Figs. 1 and 2). Independently of our test with Sc ions, the finding of a true local moment at the Fe interstitial in Yb is also strongly supported by the preliminary result of magnetism on interstitial Fe obtained for the isoelectronic and isostructural system Fe in Ca.

Combining this information with the TDPAD and IBMS results for Fe in Yb, we are able to conclude that Fe in fcc Yb metal exhibits clearly magnetic responses at both interstitial and substitutional sites [7].

We now turn to analysis and characterization of the magnetic data at the two Fe sites in terms of simple, mainly phenomenological models, which, however, yield some information beyond the scope of the LDA calculations discussed below, e.g., evidence of orbital contributions, ionic configurations, and Fe spin dynamics. As shown in Fig. 2, the local susceptibilities for both sites can be well fitted by a Curie-Weiss law, $\beta - 1 = C/(T + T_K)$, yielding a Curie constant $C = -12(2)$ K and a Kondo temperature of $T_K = 40(10)$ K for the interstitial sites, and $C = +55(5)$ K, $T_K = 40(10)$ K for the substitutional Fe sites, respectively. Furthermore, for both Fe sites the observed nuclear relaxation times τ_N are of magnetic origin without any detectable contribution from quadrupolar damping, which is consistent with cubic symmetry on both Fe sites (cf. Ref. [2]). The rates follow the Korringa relation [1], $\tau_N \propto \tau_J^{-1} \propto T$, as shown in Fig. 2. This Korringa-like behavior of the Fe $3d$ spin fluctuation rate τ_J^{-1} indicates a remarkably stable local magnetic moment for the interstitial (and substitutional) Fe sites, consistent with the small T_K values obtained (less directly) from the Curie-Weiss fits. As an additional result we note that the occupation probabilities for both Fe sites remain constant within the temperature range investigated.

According to the proportionality $C \propto B(0)$, the magnetic hyperfine field $B(0)$ for substitutional Fe is dominated by orbital contributions, which can be interpreted as being due to (unquenched parts of) the angular momentum of an ioniclike Fe $3d$ shell configuration. Thus, substitutional Fe in the divalent rare-earth metal host Yb (the conduction band of pure Yb exhibits predominantly sp character with small admixtures of $5d$ electrons) shows the typical features of ionic-type magnetism as systematically observed for Fe in sp band metal hosts [1]. In contrast, the observed negative $B(0)$ for interstitial Fe atoms is dominated by (negative) spin contact hyperfine fields. Compared to substitutional Fe, the effective suppression of orbital contributions at interstitial sites can be attributed to increased crystal field interactions and/or increased hybridization of Fe $3d$ electrons with the conduction electrons of the Yb host. It seems probable [8] that increased hybridization with $5d$ band electrons (due to increasing spatial overlap) can in turn lead to predominant spin magnetism of the more itinerant Fe $3d$ electrons and to negative $B(0)$ values—in analogy with the systematic findings for substitutional Fe in d band metal hosts [1].

These new and extreme cases of local moment formation present a challenge to theory in exploring basic features of these systems. Using the real space linear muffin tin orbital method [9], local properties of impurities in a host can be calculated without restriction to particular lattice symmetry requirements [2,5]. Because of the absence of a detectable quadrupolar damping (see above), which supports cubic symmetry around the Fe interstitial, we have focused on relaxed octahedral interstitial Fe sites in fcc Yb; this in addition is also consistent with findings for Fe in the isostructural Al lattice [10]. We have assumed unrelaxed substitutional sites; however, the inclusion of host lattice relaxation is neccessary for the interstitials. Using Lennard-Jones potentials, we have estimated the relative increase of the Fe to first-neighbor Yb distance to be most reasonably in the range from 10% to 18% of the unrelaxed impurity-first neighbor distance [7,11]. Within this range of lattice relaxations, the calculations yield magnetic behavior: a spin-polarized calculation of the local density of states (LDOS) for interstitial Fe sites gives Fe moments which increase from 0.6 to a saturation value of about $3\mu_B$ with increasing lattice relaxation. Figure 4 shows LDOS curves for Fe interstitials with 14% relaxation, yielding an Fe moment of $2.2\mu_B$, as well as for (unrelaxed) substitutional Fe with a (spin only) moment of $3.14\mu_B$. Furthermore, we have calculated the isomer shifts, finding a positive value of $+0.24$ mm/s for substitutional and (depending on the lattice relaxation) negative values in the range of -0.22 to -0.34 mm/s for interstitial Fe. The unusual sensitivity to lattice relaxation of the calculated isomer shift at interstitial sites is mainly due to the critical buildup of magnetism, affecting the electronic structure via the spin polarization. Larger relaxations increase the Fe moment and tend to induce a

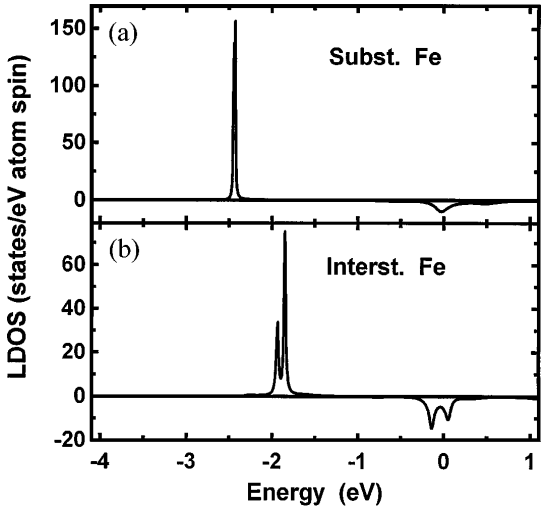

FIG. 4. Local spin densities of states calculated for (a) substitutional and (b) 14%-relaxed octahedral interstitial Fe impurities in fcc Yb. Energies in eV are given relative to the Fermi level of Yb.

more negative isomer shift, which approaches the experimental value at relaxations above 12%. All these theoretical results on magnetism and isomer shift are consistent with the experimental findings, which in turn also give some support for the assumption of octahedral interstitial Fe sites with the estimated degree of lattice relaxation.

Of special relevance for the mechanism of local moment formation at interstitial (and substitutional) Fe sites are the calculated LDOS curves. The non-spin-polarized calculations yield sufficiently high LDOS at the Fermi energy, $N(E_F)$, for both Fe sites in Yb to fulfill the local Stoner criterion for the existence of a local moment, $N(E_F)I > 1$. For interstitial sites, the necessary high density of states arises from the presence of a surprisingly sharp Fe $3d$ peak, close to the Fermi level [5]. Sharp peaks are also apparent in the spin-polarized LDOS of Fig. 4.

In summary, by combining the results of two nuclear methods, we have provided evidence for the existence of magnetism at an interstitial $3d$ ion in a metal. As deduced from the Curie-Weiss behavior of the susceptibility and the Korringa-like spin dynamics, interstitial Fe in Yb develops a stable local moment with negative $B(0)$ and spin dominated magnetism, in contrast to substitutional Fe with positive $B(0)$ and ionic-type magnetism. Theoretical predictions based on the LSD approximation are (somewhat surprisingly) consistent with the experimental findings at both Fe sites. Moreover, the theoretical results support the assumption of octahedral interstitial Fe sites and give basic insight into the electronic structure and mechanism of local moment formation, in particular at the interstitial site.

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[8] We note that this line of reasoning can be tested by theory, which indicates for interstitial Fe significant crystal field interactions and more prominent Fe $3d$-Yb $5d$ hybridization (see Fig. 4 for an impression).
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